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Liquid Phase Deposition of TiO_2 Films for Electron Transport Layer of Perovskite Solar Cells

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The TiO_2 layer plays an important role in organic lead-halide perovskite solar cells (PSCs) as an electron transport layer as well as a blocking layer to prevent carrier recombination at the interface of fluorine-doped tin oxide (FTO) and a perovskite layer. TiO_2 thin film was successfully grown on FTO substrate using the liquid phase deposition method. In this work, TiO_2 layers were grown at a temperature of 50 °C. The first layer was grown for 2 h and the second layer was subsequently grown at different durations, i.e. 1, 2, 3, and 4 h. The optical, structural and morphological properties of the samples were characterized using UV-vis spectroscopy, XRD and FESEM/EDX, respectively. The TiO_2 thin film was then applied as an electron transport material (ETM) in the PSC *n-i-p* configuration. The UV-vis characterization results showed that the peak absorption spectrum of TiO_2 thin films occurred in the wavelength range of 300-450 nm for all samples. The XRD pattern indicated that the sample is anatase TiO_2 structure with the crystal orientation of (100), (004), (200) and (105) at the diffraction peak angle of 2θ: 25.50°, 37.92°, 48.04° and 54.84°, respectively. FESEM characterization showed that the TiO_2 nanostructure has a rod-like morphology. The PSC device fabricated utilizing the TiO_2 sample with a second layer grown for 2 h exhibits the highest power conversion efficiency of 0.23 %.

Keywords: TiO_2, Liquid phase deposition, Electron transport material, FESEM, Perovskite solar cell.

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1. INTRODUCTION

Perovskite solar cell (PSC) is a new generation of solar cells with promising performance as a result of excellent photophysical properties of the organo-lead halide perovskite materials. Initially, Miyasaka group applied $CH_3NH_3PbI_3$ organometal halide perovskite over TiO_2 as a substitute for light-absorbing material (dye) on DSSC and successfully achieved a cell efficiency of 3.8 % [1]. The device of PSCs has been developed based on the organic lead halides or mixed halides perovskites, e.g. $CH_3NH_3PbI_3$ or $CH_3NH_3PbI_{3-x}Cl_x$ by another research group [2]. The power conversion efficiency (PCE) of PSCs has rapidly increased in the past few years from 9 to 22.1 % [3]. In general, PSCs consist of an electron transport layer (ETL), perovskite layer and hole transport layer (HTL). The high-performance PSCs commonly used TiO_2 thin film as ETL incorporating $CH_3NH_3PbI_3$ perovskite as a light absorber material [3].

There are two types of TiO_2 used as an ETL in PSC in terms of its porosity, i.e. compact and mesoporous TiO_2. The compact TiO_2 layer will transfer photogenerated electrons from perovskite and, at the same time, it will act as a blocking layer to prevent direct contact between a hole and FTO which results in a decrease in cell efficiency [4]. The mesoporous TiO_2 is preferable to gain more contacts between ETL and the organic perovskite material [2]. The properties, structure and morphology of TiO_2 are strongly dependent on the preparation technique. The preparation method may influence the morphology and structure of TiO_2 film and indirectly influence the power conversion efficiency of solar cells. Several techniques have been reported to fabricate TiO_2 as ETL, e.g. the hydrothermal method [5], screen-printing [6], DC magnetron sputtering, natural dropping [7] and sol-gel followed by spin-coating [8]. In many cases, those methods required expensive equipment and complicated procedures to obtain a required nanostructure of TiO_2. The liquid phase deposition (LPD) method is a simple wet-chemical process to grow metal oxide thin film. The liquid phase deposition method has the advantage that can be carried out under atmospheric conditions at room temperature without using any special equipment [9]. The LPD can be done by reacting metal-fluoro complex with fluor anion scavenger of boric acid [10]. In this paper, the LPD technique has been employed to fabricate rod-like TiO_2 nanostructure without any directing agent. TiO_2 thin layers were fabricated in various growth times and then applied as ETL in PSC. The effect of variation in growth time on the optical properties, morphology, structure, and efficiency of PSC was then analyzed and discussed.

2. EXPERIMENTAL

2.1 Material and Method

Ammonium hexafluortitanate ($(NH_4)_2TiF_6$) (AHT), boric acid (H_3BO_3), lead (II) oxide (PbI_2), poly[bis(4-phenyl) (2,4,6trimethylphenyl)amine] and fluorine-doped tin oxide (FTO) glass were purchased from Sigma Aldrich and methylammonium iodide ($(CH_3NH_3)I_2$) was supplied from Dyesol Ltd. Australia. $(NH_4)_2TiF_6$ and H_3BO_3 were used as precursors and anion scavenger, respectively, for the synthesis of TiO_2. PbI_2 and methylammonium iodide were used as a starting material for

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synthesis of organo-metal halide $CH_3NH_3PbI_3$ perovskite. Poly[bis(4-phenyl) (2,4,6trimethylphenyl)amine] (PTAA) was used for the hole transport material (HTM), while dimethylformamide was used as solvent. Fisrt, the FTO substrate was cut and cleaned by consecutive ultrasonication in acetone, ethanol and deionized water. The preparation procedure of TiO_2 thin films referred to the method published previously [9]. Typically, 5 ml of 0.1 M $(NH_4)_2TiF_6$ and 5 ml of 0.2 M H_3BO_3 aqueous solution were mixed and then used as a growth solution. The FTO substrate was placed vertically in the growth solution at a temperature of 50 °C. The TiO_2 films were grown twice with the same growth condition. For all samples, the first layer was grown for 2 h. The second layers were grown at different times, i.e. 1, 2, 3 and 4 h. The prepared thin film of TiO_2 was then taken out of the solution, washed with an abundant of DI-water, dried with nitrogen flow and annealed at 400 °C for 30 min. The samples were named according to their first (x) and second (y) growth time in hours, i.e. Tx-y. The organic perovskite coating was done by the two-step method. In the first step, 400 mg/ml of PbI_2 in dimethylformamide was spin-coated onto the TiO_2 layer at a speed of 3000 rpm for 10 s. This layer was then annealed at 100 °C for 5 min. In the second step, 40 mg/ml of methylammonium iodide (MAI) in 2-propanol was spin-coated at a speed of 3000 rpm for 10 s. The samples were then annealed at 100 °C for 30 min. The HTM layer is prepared by spin-coating 20 mg/ml PTAA on the perovskite layer. Samples were annealed at 100 °C for 10 min. The final step was fabricating metal electrodes by sputtering the platinum metal over the sample with an active area of 0.23 cm^2.

2.2 Characterization

Optical properties of thin films were characterized using Hitachi U-3900H UV-vis spectroscopy (Lambda 900 Perkin-Elmer) and surface morphology was characterized by Field-Effect Electron Scanning Microscopy (FESEM) (Zeiss SUPRA 55VP). The structure and crystallinity of the samples were characterized using X-ray diffraction (BRUKER D8 Advance) with CuKα radiation (λ = 0.154 nm) and a scan step of 2°/min. The PSC performance utilizing the samples with various growth times was recorded by high-voltage source (Keithley model 237). The current-voltage measurements were carried out under AM 1.5 simulated light illumination with an intensity of 100 mW/cm^2.

3. RESULTS AND DISCUSSION

Fig. 1 shows the UV-visible optical absorption spectrum of TiO_2 sample grown using a liquid phase deposition method with different growth times. The UV-vis absorption spectrum of the sample shows the dominant absorption peak in the UV region. The absorption peak occurs in the range of wavelengths 300-350 nm [11]. This result was also observed in [12]. The sample prepared without the second layer (T2-0) possesses the lowest absorption peak in the UV light range, while the highest absorption peak belongs to the sample prepared for 3 h of second-growth time (T2-3). It is also obvious that the absorption area varies with the growth time of the secondary layer. The sample prepared for 4 h of the second layer (T2-4) demonstrates the largest absorption area, and the sample without the secondary layer (T2-0) has the smallest absorption area. The peak of UV-vis absorption of TiO_2 layer that grew more than 1 layer was observed to shift towards larger wavelengths and was at a wavelength of around 350-380 nm (near visible light).

The magnitude of the energy band gap of all the samples was calculated. The UV-vis absorption spectrum produced by semiconductor samples provides a correlation between the absorbance and the photon energy needed to excite the electrons from the valence band to the conduction band. The relationship between the photon beam energy of excitation and the band gap energy (band gap, E_g) is given by the Tauc equation:

$$(Ah\nu)^n = A \cdot (h\nu - E_g). \quad (1)$$

The power of n for indirect energy gap is equal to 1/2 and 2 for direct energy gap. The energy of the optical band gap E_g for TiO_2 is obtained by extrapolating the curve $h\nu$ vs $(\alpha h\nu)^{1/2}$. The intercept of the straight line for the x-axis is defined as the value of E_g (Fig. 1b). The value of energy gap for all the samples is listed in Table 1.

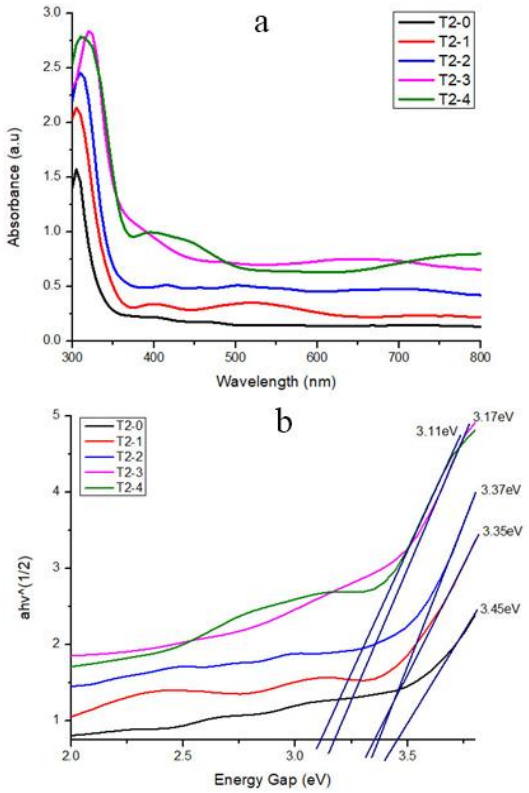

Fig. 1 – UV-vis spectra (a) and energy band gap calculation (b)

Table 1 – Energy band gap of TiO_2 at different growth times

No	Sample	Energy band gap (eV)
1	T2-0	3.45
2	T2-1	3.35
3	T2-2	3.37
4	T2-3	3.17
5	T2-4	3.11

Fig. 2a, f show the top view FESEM images of TiO_2 samples grown for 2 h (T2-0) as a basis layer with 1.000 and 50.000 times magnification, respectively. Fig. 2b-e are FESEM images of the sample subsequently grown for the second layer for 1, 2, 3 and 4 h at a temperature of 50 °C. It is obviously noticed that the morphological shape of the sample changes with growth time. It can be seen that for 2 h of growth time, the TiO_2 rod-like structure has been obtained. This result agrees well with the morphology of TiO_2 film prepared by LPD by Umar and his group [9]. As the first layer subjected to the second-growth process, it can be seen that the precursor initiates another structure on the surface [12]. As the growth time for the second process increases, a bigger grain size was obtained. FESEM images of as-deposited films observed the existence of cracks. Cracks generally occur due to the intrinsic high surface tension of the TiO_2 layer [9].The presence of the crack might increase the porosity of the film.

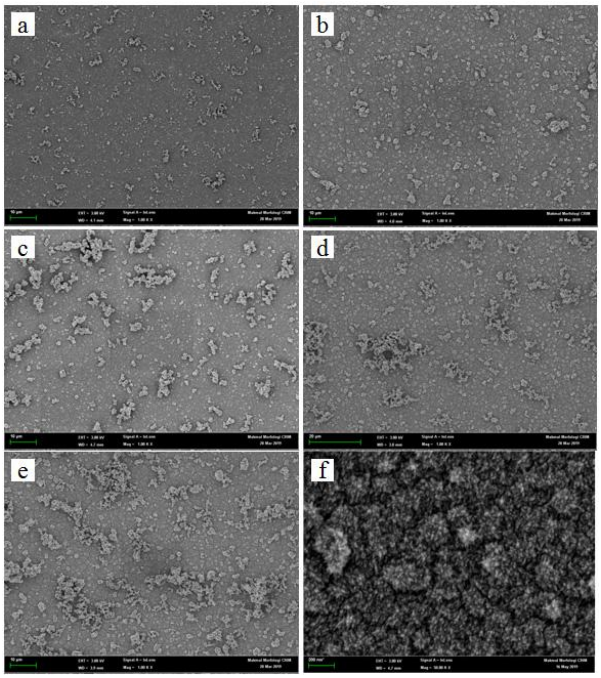

Fig. 2 – FESEM image of the samples: T2-0 (a), T2-1 (b), T2-2 (c), T2-3 (d), T2-4 (e), T2-0 (f) with magnification of 50.000x

The EDX spectrum of sample T2-0 is shown in Fig. 3. The picture also displays the percentage of the weight of the constituent atoms contained in the sample. Based on EDX data, there are elements Sn, C and Si in the sample. The Ti and O content in TiO_2 sample with the growth time of 2 h (T2-0) are 9.4 and 27.77 (wt. %), respectively. The appearance of Sn element comes from the FTO substrate due to the fact that T2-0 is the sample with the thinnest layer, with a percentage of atomic weight of 59.7 %. In addition, there are also carbon and silica elements derived from combustion (annealing), each of which has a percentage of atomic weight of 2.7 % and 0.6 %, respectively.

Fig. 4 shows the XRD spectra of two selected samples, i.e. single layer and double layer samples, namely T2-0 and T2-4, respectively. It indicates that sample T2-0 (single layer) still reveals strong diffraction from FTO. After the addition of the second layer grown for 4 h, that is sample T2-4, strong diffraction from (101) plane was observed, which agrees with the JCPDS card file no. 96-900-9087 [13].

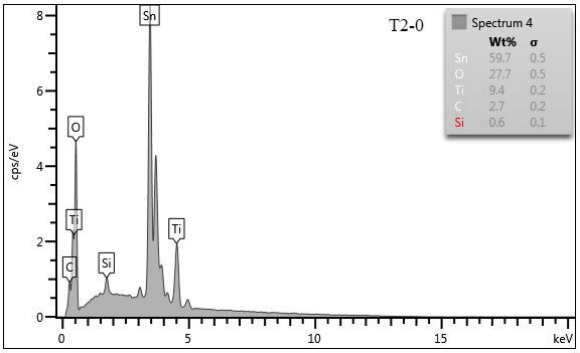

Fig. 3 – EDX spectrum of TiO_2 with growth time of 2 h

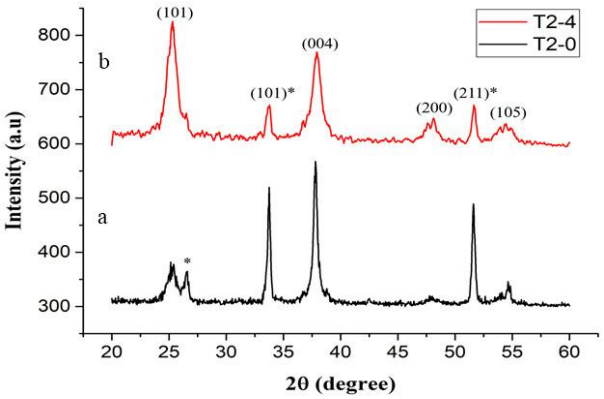

Fig. 4 – XRD spectrum of TiO_2 with growth time of 2 h

Table 2 – Material properties used in this study

Sample	β (°)	FWHM (rad.)	Crystallite size (nm)
T2-0	37.92	0.464	29.56
T2-4	38.20	0.942	14.56

Thus, X-ray diffraction peaks at 25.50°, 37.92°, 48.04°, and 54.84° correspond to (101), (004), (200), and (211) plane of anatase TiO_2, respectively. The calculated lattice parameters of anatase TiO_2 are $a = 0.37796$ nm and $c = 0.94858$ nm. Anatase-TiO_2 is preferable to be applied as an electron transport layer in PSC due to its high photoactivity properties. The crystalline size can be calculated from the FWHM value of X-ray diffraction peak using the Scherrer's formula. The FWHM values of (400) plane of T2-0 and T2-4 samples were obtained using the Origin Pro 2016. FWHM values and calculated crystallite sizes are listed in Table 2. According to XRD spectra, T2-0 sample has a large crystallite size compared to the T2-4 sample in [400] direction. Constructive interference that occurs due to the crystalline plane will be higher if the crystalline size is also large.

Fig. 5a, b demonstrate the *J-V* curve of the fabricated PSC device using TiO_2 film grown with different growth times in dark and under 100 mW/m^2 illumination, respectively. In dark conditions, the *J-V* curves show typical semiconductor diode characteristics. The smaller the potential difference required by the electron to be excited (a rapid increase in current), the better the solar cell will work.

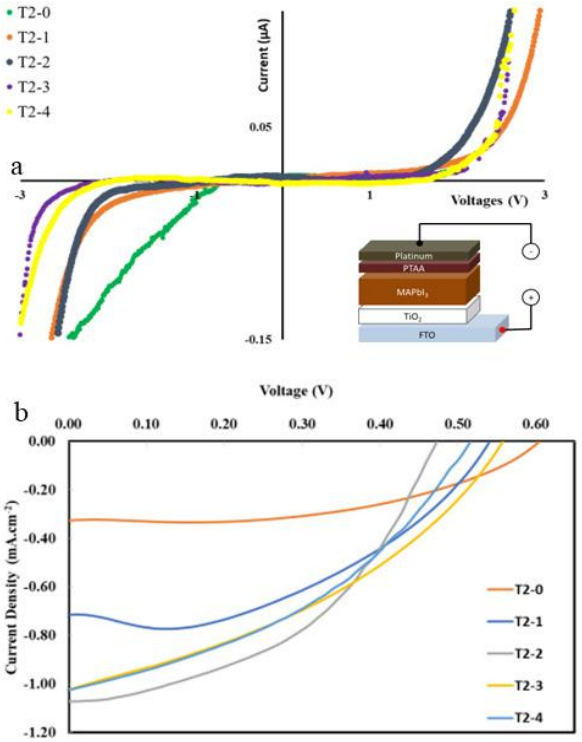

Fig. 5 – *J-V* curve (a) in dark and cell configuration for the PSC performance measurement (insert) and (b) under illumination of 100 mW/m² for the PSC with different growth time of TiO_2

The thickness of the ETM was found to influence the PSC performance, as expected. We assumed that TiO_2 electron selective growth time is related to their layer thickness. Table 3 summarizes the photovoltaic properties of PSC utilizing LPD prepared TiO_2 samples based on the *J-V* curves from Fig. 5b. Sample with a single TiO_2 layer (T2-0) has the highest open-circuit voltage (V_{oc}) but the lowest short-current density (J_{sc}) and the lowest efficiency, i.e. 0.1 %.

Addition of the second layer grown for 1 h has significantly increased the efficiency up to 0.19 %. The sample prepared by double layer deposition for 2 and 2 h (T2-2) possesses the lowest V_{oc} but the highest *Isc* and resulted in the highest solar cell efficiency, i.e. 0.23 %.

Table 3 – Measurement data and calculation of PSC based on TiO_2 with variations in growth temperature

Sample	V_{oc} (V)	J_{sc} (mA/cm²)	FF	η (%)
T2-0	0.56	0.329	0.526	0.10
T2-1	0.54	0.720	0.483	0.19
T2-2	0.47	1.071	0.453	0.23
T2-3	0.55	1.033	0.377	0.22
T2-4	0.51	1.036	0.395	0.21

4. CONCLUSIONS

In this work, TiO_2 thin films were successfully grown on FTO by using the liquid-phase deposition method with various growth times and were applied as an electron transport material to the PSC device. It was observed that the morphology and the optical absorbance of the samples were influenced by the TiO_2 growth time. The highest J_{sc} of 1.071 and η of 0.23 % were obtained for PSC utilizing the sample grown at 50 °C for 2 h each.

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Осадження рідкої фази плівок TiO_2 для електронно-транспортного шару перовскітних сонячних елементів

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Шар TiO_2 відіграє важливу роль в органічних свинцево-галогенідних перовскітних сонячних елементах (PSCs) як електронно-транспортний шар, а також як блокуючий шар для запобігання рекомбінації носіїв на межі поділу легованого фтором оксиду олова (FTO) та перовскітого шару. Тонку плівку TiO_2 успішно вирощували на підкладці FTO методом осадження рідкої фази. У цій роботі шари TiO_2 вирощували в два заходи при температурі 50 °C. Перший шар вирощували протягом 2 год, а другий шар згодом вирощували з різною тривалістю, а саме протягом 1, 2, 3 та 4 год. Оптичні, структурні та морфологічні властивості зразків характеризували відповідно за допомогою УФ-спектроскопії, XRD та FESEM/EDX. Потім тонку плівку TiO_2 застосовували як електронно-транспортний матеріал (ETM) у PSC з конфігурацією *n-i-p*. Результати УФ-спектроскопії показали, що спектр максимального поглинання тонких плівок TiO_2 відповідає діапазону довжин хвиль 300-450 нм для усіх зразків. На дифрактограмі виявлено, що зразок є структурою анатазу TiO_2 з кристалічною орієнтацією (100), (004), (200) і (105) при кутах пікової дифракції 2θ, рівними відповідно 25,50°; 37,92°; 48,04° і 54,84°. FESEM характеристика показала, що наноструктура TiO_2 має стрижнеподібну морфологію. Пристрій PSC, виготовлений з використанням зразка TiO_2 з другим шаром, вирощеним протягом 2 год, демонструє найвищу ефективність перетворення потужності, рівну 0,23 %.

Ключові слова: TiO_2, Осадження рідкої фази, Електронно-транспортний матеріал, FESEM, Перовскітні сонячні елементи.