Optimization of Spin Coated TiO$_2$ Layer for Hole-Free Perovskite Solar Cell

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Abstract. The optimization of the TiO$_2$ layer in free-hole perovskite solar cells is critical, as it strongly affects the device performance. In this study, simple FTO/TiO$_2$/CH$_3$NH$_3$PbI$_3$/C solar cells were fabricated, via two-step dipping method, with different thickness of TiO$_2$ layer. The structure and microstructure of the TiO$_2$ layers were investigated by X-Ray diffraction (XRD), Raman spectroscopy, and UV spectroscopy (UV-Vis). The effect of different TiO$_2$ thickness on the structure and photovoltaic performance of the fabricated devices were investigated using XRD and IV measurement, respectively. The photovoltaic parameters, including short-circuit-current (J$_{sc}$), open-circuit-voltage (V$_{oc}$), Fill factor (F.F) and power conversion efficiency (PCE), were found to be strongly dependent on the thickness of TiO$_2$ layer. The investigation showed that, efficient device can be fabricated by optimizing the TiO$_2$ thickness, employing a thickness of 108 nm as an optimum thickness in this study.

Keywords: Perovskite, CH$_3$NH$_3$PbI$_3$, TiO$_2$, Solar cell.

1. Introduction

Recently, the organic–inorganic perovskite CH$_3$NH$_3$PbI$_3$ has attracted new and promising class of materials for photovoltaic applications due to their large absorption coefficient, high carrier mobility, longer free charge carrier lifetimes and broad range of light absorption [1–11]. The advantages of low cost, facile fabrication and high-power conversion efficiency (PCE) make perovskite solar cells (PSCs) competitive with conventional silicon based solar cells [12,13]. Typically, PSCs are composed of five parts: conductive glass (FTO or ITO), electron transport layer (ETL), a perovskite absorber layer, hole transport layer (HTL) and counter electrode (Au, Ag or C).

The electron transport layer (ETL) is indispensable and plays an important role in the performance of PSCs. It is responsible for extracting the photogenerated electron from the perovskite layer and transporting these electrons to the external circuit. In addition, prevent the holes generated in the perovskite from reaching the conductive glass to avoid short circuit [14–16]. Therefore, high transparency, good charge collection capability, suitable bandgap and appropriate thickness of ETL contribute significantly to the reduction of carrier recombination and hence the performance of the PSCs.

Several organic and inorganic materials have been used as electron transport layers, such as ZnO, SnO$_2$, CsCO$_3$, PCBM and TiO$_2$ [17–22]. Among these materials, TiO$_2$ is the most widely used as an ETL because of its environmentally friendly nature, wide band gap, high electron mobility and good stability [23–26]. The compact TiO$_2$ layer can be produced either by spin coating, spray pyrolysis, atomic layer deposition (ALD), electrochemical deposition or thermal oxidation [8,27–33]. Among them, spin coating is considered as the simplest and more cost-effective method for depositing TiO$_2$ layers, where a TiO$_2$ precursor solution is spread onto a FTO substrate and spun to form a thin transparent film. In particular, the crystallographic form, surface modification, temperature treatment and the film thickness of the TiO$_2$ layer have a great influence on the crystallinity and thickness of the perovskite layer and hence the performance of the PSC [16,34–36].

Herein, it is interesting to investigate the effect of TiO$_2$ thicknesses (using spin coating method) on subsequently deposited perovskite film and the photovoltaic performance of the PSCs. In the aim of simplifying the cell
structure besides reducing the manufacturing cost, hole-free perovskite solar cells were fabricated using a commercial carbon paste, as a counter electrode, instead of Au and Ag.

2. Materials and methods

2.1. TiO₂ samples preparation

Initially, the fluorine-doped tin oxide (FTO) glass substrates were etched with HCL and Zinc powder. The substrates were ultrasonically cleaned for 10 minutes in each of: acetone, isopropanol and de-ionized water, to remove any traces of impurities, then air dried.

To prepare the TiO₂ precursor solution, a solution consisting of 175 μL of titanium (IV) isopropoxide in 1.25 mL of anhydrous isopropanol was added to a solution of 17.5 mL of HCl in 1.25 mL of anhydrous isopropanol [37].

The spin-coating of the TiO₂ solution was carried out in air at 3500 rpm for 30 s and consequently dried at 240 °C for 1 min. The thickness of the TiO₂ layer was tuned by adjusting the number of the above spinning-drying cycle. Subsequently, the resulting films were annealed in air at 450 °C for 45 min. The films with 1, 3, 6, 9, and 12 spin-coated layers were denoted 1X, 3X, 6X, 9X and 12X, respectively.

2.2. Device fabrication

The two-step solution deposition, as a facile and low-cost method, was used to fabricate the perovskite cells [8]. PbI₂ solution (1 M) was prepared by dissolving 462 mg PbI₂ in 1 ml N,N-dimethylformamide under stirring at 70 °C. The different TiO₂ films were infiltrated with PbI₂ by spin-coating a PbI₂ solution at 6000 rpm for 30 s. The obtained films were then annealed at 70 °C for 30 min. After cooling to room temperature, the films were dipped in a solution of CH₃NH₃I in isopropanol (10 mg ml⁻¹) for 20 s and rinsed with isopropanol. Finally, once the perovskite film cooled down to room temperature, the commercial carbon paste was deposited on the films by doctor-blading technique and dried at 100 °C for 30 min.

2.3. Characterization

X-ray diffraction patterns of the samples were collected on a Philips diffractometer (X'pert MPD). The diffracted intensities were collected using Cu Kα radiation of a copper sealed tube charged with 40 kV voltage and 30 mA. To correct instrumental broadening, LaB₆ standard was used. The crystalline structure of the TiO₂ film was studied using Raman spectroscopy by using HORIBA JOBIN YVON Ramanor HG2S spectrometer, equipped with a micro-Raman attachment and Ar+ laser excitation (514.5 nm).

The optical properties of TiO₂ films were studied using ultraviolet-visible spectroscopy (UV–vis). The diffuse reflectance spectra of the TiO₂ thin films, were obtained using a Shimadzu UV-2700 UV–vis spectrophotometer in the wavelength range from 300 nm to 800 nm.

The current density-voltage (J-V) characteristics of PSC devices were measured in air with a digital source meter (Keithley 2400) under one-sun illumination (AM 1.5 G, 100 mW cm⁻² at 25 °C) from a solar simulator (Sol3A Class AAA). The cross-section morphology of perovskite cell was investigated by using a scanning electron microscope (SEM, Quanta FEG 250) at 20 kV.

3. Results and Discussion

XRD pattern of the Glass/TiO₂ thin film is shown in Figure 1. The phase identification ratifies the formation of a Tetragonal anatase TiO₂ (ICDD: 01-089-4921). The inset shows the main peak, (101), for the TiO₂ films of different layers. As shown, the peak intensity is enhanced as the number of layers increased; which is an indicator for increasing the film thickness. This is due to the fact that the diffracted intensity is highly affected by the film thickness. Moreover, increasing the number of layers lead to a slight reduction in the integral breadth which gave rise to an increase in the crystallite size. The average crystallite sizes of TiO₂ particles for the different films were estimated using Scherrer formula, given by
where $D$ is the crystallite size, $k$ is a constant, $\lambda$ is the x-ray wavelength (0.1540 nm), $\beta$ is the integral breadth of the diffraction peak. For more realistic calculation, the broadening of the glass substrate was deconvoluted. The calculations estimated an average crystallite size of 8, 11, 13, 14 and 17 nm±2 for the film coated by one layer (1X), three layers (3X), six layers (6X), nine layers (9X) and twelve layers (12X), respectively.

In order to confirm the anatase phase for the TiO$_2$ film, Raman spectroscopy was performed and a Raman bands at 398, 517, 640 and 798 cm$^{-1}$ were obtained, Figure 2. The obtained bands are a characteristic bands for the anatase phase. The bands at 640 cm$^{-1}$ is assigned to the E$_g$ mode and the band at 398 cm$^{-1}$ to the B$_{1g}$ mode. The band at 517 cm$^{-1}$ is a doublet of the A$_{1g}$ and B$_{1g}$ modes. The weak band at 798 cm$^{-1}$ is the first overtone of the B$_{1g}$ mode.

![Figure 1. The XRD of TiO$_2$ film. Inset shows the XRD of (101) plane for different TiO$_2$ films (The number before “X” in the legend indicates the number of TiO$_2$ layers spin coated on the substrate)](image)

![Figure 2. Raman Spectrum of TiO$_2$ film. (One-layer TiO$_2$ film,1X)](image)
mode.

Figure 3 shows the variation of the optical absorbance versus wavelength for the TiO$_2$ thin film samples, in the wavelength range between 200 nm and 800 nm. The graphs show that the absorbance decreased sharply in the 300–350 nm wavelength range and then become relatively constant. From the plot, it is obvious that the absorbance of the films goes on increasing with increment the number of spin coating cycle owing to increased film thickness. Furthermore, the absorption edge shifts towards longer wavelengths indicating a decrease in the band gap as a result of increasing the crystallite size.

![Absorbance spectra of TiO$_2$ thin film samples](image)

**Figure 3.** The optical absorbance for TiO$_2$ thin film samples.

The most common method to calculate the optical band gap for the thin films is fitting the data to Tauc’s relation of the form [38],

$$ahv = \beta (hv - E_g)^n$$

where, $hv$ is the incident photon energy, $E_g$ is the optical band gap, $\beta$ is a constant that depends on the transition probability and $\alpha$ is the absorption coefficient which is computed from the absorbance ($A$) using the equation ,

$$\alpha(\lambda) = \frac{2.303 A(\lambda)}{t}$$

where $t$ is the film thickness. The exponent $n$ takes different values depending on the mechanism transitions, which is 1/2 for direct and 2 for indirect allowed transitions.

Absorption spectrum fitting (ASF) method is another powerful method used to determine the optical band gap [39,40]. This method depends on the variation of the optical absorbance versus wavelength of the material only without the need of the film thickness. In this procedure, Tauc’s relation can expressed as a function of the wavelength ($\lambda$):

$$\frac{A(\lambda)}{\lambda} = C \left( \frac{1}{\lambda} - \frac{1}{\lambda_g} \right)^n$$

Where

$$C = \beta \left( \frac{h c}{2303} \right)^{\frac{1}{n-1}}$$

Here, $h$, $c$ and $\lambda_g$ are Planck’s constant, the velocity of light and the wavelength corresponding to the optical bandgap, respectively. This equation could be used to estimate the optical band gap without the need of the film thickness. The value of the band gap in eV can be calculated from the parameter $\lambda_g$ using

$$E_g^{ASF} = 1240 / \lambda_g$$
The value of $\lambda_g$ can be determined by extrapolating the linear part of $\left( \frac{A}{g} \right)^{1/n}$ versus $\left( \frac{1}{g} \right)$ curve at $\left( \frac{1}{g} \right) = 0$.

Figure 4 shows the ASF plot for the films coated once, 1X, and 3X, 6X, 9X and 12X. As a benefit of ASF method, the slope of the straight line for the linear region is a good indicator for the change of the film thickness. It is observed that, as the number of coating cycle increases, the slope increases, indicating an increase in the film thickness, Figure 4 (f).

Using the fitting parameters, the band gap energies for the film coated by one layer(1X), three layers (3X), six layers(6X), nine layers(9X) and twelve layers(12X) are 3.28, 3.26, 3.25, 3.25 and 3.25 eV, respectively. It is obvious that, with the increase in the film thickness, band gap slightly decreases as a consequence of increasing the crystallite size.

The XRD patterns for CH$_3$NH$_3$PbI$_3$ based on one (1X), three (3X), six (6X), nine (9X) and twelve (12X) TiO$_2$ layers are displayed in Figure 5. The CH$_3$NH$_3$PbI$_3$ films gives diffraction peaks at 14.14, 20.05, 23.53, 24.53, 28.50, 31.95, 40.54 and 43.11°, which are assigned to the (110), (020), (121), (022), (220), (130), (224) and (134) planes of the tetragonal (I 4 c m) perovskite structure with $a = 8.85$ Å and $c = 12.63$ Å. In addition, an additional diffraction peaks at 26.48, 33.74 and 37.80° which are assigned to the (110), (101) and (200) planes of the tetragonal SnO$_2$. Besides a peak at 12.66° which is belong to the (001) plane of the Hexagonal PbI$_2$.

Figure 6 shows the dependence of the diffraction intensities of both (110) plane of CH$_3$NH$_3$PbI$_3$ and (001) plane of PbI$_2$ on the TiO$_2$ thickness. It is obvious that, by increasing the TiO$_2$ thickness, the diffraction intensity of both (110) plane of CH$_3$NH$_3$PbI$_3$ and (001) plane of PbI$_2$ increases. The increase in the CH$_3$NH$_3$PbI$_3$ diffraction intensities might attributed to the thicker TiO$_2$ which give rise to more PbI$_2$ absorbed and therefore thicker CH$_3$NH$_3$PbI$_3$ film formed. Meanwhile, the ratio of PbI$_2$ to CH$_3$NH$_3$PbI$_3$ intensities increases, which is indication for increasing the amount of un-reacted PbI$_2$.

**Figure 4.** ASF plot for the TiO$_2$ film spin coated by a) one layer(1X) , b) three layers (3X) , c) six layers(6X) , d) nine layers(9X) and e) twelve layers(12X) . f) Slope as a function of number of layers
The typical J-V curve of the best-performing devices based on one (1X), three (3X), six (6X), nine (9X) and twelve (12X) TiO2 layers are shown in Figure 7. In order to ensure the reliability of our results, for each TiO2 thickness, we fabricated 3 devices each containing 3 cells and tested under the same conditions. The corresponding average photovoltaic parameters, including open-circuit potential (Voc), short-current density (Jsc), Fill factor (FF) and PCEs, are shown in Figure 8.

The average short-circuits current for PSCs with one (1X), three (3X), six (6X), nine (9X) and twelve (12X) TiO2 layers are 4.785 mA/cm², 6.465 mA/cm², 7.2 mA/cm², 5.7 mA/cm² and 5 mA/cm², respectively. While the open-circuit voltage are 0.64 V, 0.8 V, 0.82 V, 0.75 V and 0.64 V, respectively.

Figure 5. The XRD patterns for CH3NH3PbI3 based on different TiO2 layers. (a) one layer (1X), (b) three

Figure 6. Diffraction peaks for (001) of PbI2 and (110) of CH3NH3PbI3 for different TiO2 based films
We found that the $J_{sc}$ increased with increased the number of TiO$_2$ layers until 6 layers but decreased for devices with nine and twelve TiO$_2$ layers. For the devices with one, three and six TiO$_2$ layer, the increase in the $J_{sc}$ might attributed to the increase of the surface roughness which give rise to enhance the interfacial area and therefore the rate of electron transfer. Moreover, increasing number of TiO$_2$ layers may result in absorbing more PbI$_2$ and therefore a relative thicker CH$_3$NH$_3$PbI$_3$ is formed, as demonstrated by XRD.

Upon increasing the number of TiO$_2$ layers, nine and twelve layers, the $J_{sc}$ decreased, we speculate that might be due to the effect of charge accumulation in the TiO$_2$/CH$_3$NH$_3$PbI$_3$ interface that obstructs the interfacial electron transfer on the surface of the TiO$_2$ layer, as result of the un-reacted PbI$_2$. In addition, the conductivity of TiO$_2$ might be a problem for a thicker film.

The trend of the average open circuit voltage ($V_{oc}$) and the average fill factor (FF) is similar to that of the average short circuit current ($J_{sc}$). The drop in the open circuit voltage can be explained based on the classic theory model [41,42], the $V_{oc}$ is related to the ETL thickness by

$$V_{oc} = -A \ln d + B$$

Where $d$ is approximately the average thickness of the (ETL) and the terms A and B are depending on the absorption Coefficient, thickness, charge generation efficiency, thermal activation energy, recombination constant of the perovskite film, etc. Assuming A and B are constant, which don’t vary with the TiO$_2$ thickness, $V_{oc}$ is inversely proportional to the TiO$_2$ thickness. Furthermore, the illuminated light would be scattered strongly by the thick film, resulting in a great loss of light energy when passing through the film, leading to decrease the average photogenerated carrier and hence the $V_{oc}$ [42].

Figure 8(b) show that, the devices with six TiO$_2$ layers exhibit the best PCE among the five devices, 2.55%, with $V_{oc}$ (0.82 V), $J_{sc}$ (7.2 mA/cm$^2$) and FF (43.2%). The best performance is attributed to good surface roughness, thicker CH$_3$NH$_3$PbI$_3$ layer and low recombination rate.

![Figure 7](image)

**Figure 7.** J-V curves of the PSCs based on different TiO2 thicknesses: (a) one layer, (b) three layers, (c) six layers, (d) nine layers and (e) twelve layers.
In order to obtain the TiO$_2$ thickness, Scanning Electron microscope SEM is used. Figure 9 shows the cross-section SEM image of FTO/TiO$_2$/CH$_3$NH$_3$PbI$_3$ film that with 6 layers of TiO$_2$. The thickness of the TiO$_2$ layer is approximately 108 nm while that of the CH$_3$NH$_3$PbI$_3$ perovskite is about 332 nm.

4. Conclusion

In summary, The Spin coating technique was used to prepare a compact TiO$_2$ layer with different thicknesses. A perovskite solar cells with structure FTO/TiO$_2$/CH$_3$NH$_3$PbI$_3$/C were prepared based on different thicknesses of TiO$_2$ layer. The thicker TiO$_2$ layer was found to result in absorbing more PbI$_2$ and therefore relative thicker CH$_3$NH$_3$PbI$_3$. We have studied how the TiO$_2$ layer thickness influences the photovoltaic performance of the perovskite solar cells. The J-V curves revealed that the photovoltaic performance of PSCs could be appropriated with TiO$_2$ layer of thickness 108 nm.
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