



Mesoporous TiO₂-layer's rheological impact on the perovskite solar cell performance

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ABSTRACT

The rheological impact of the mesoporous-TiO₂ (m-TiO₂) layer was investigated, which impacted perovskite solar cell (PSC) performance. This also implies the significance of morphological variations according to the pastes' viscosity and corresponding thickness that cause a slight influence on their bandgap and hence device photovoltaic performance. The m-TiO₂ paste results in a viscosity of 2.85 cP with a thickness of 1 μm, indicating the bandgap of ~ 3.55 eV. In contrast, the higher viscous paste (3.85 cP) exhibits a slightly enhanced bandgap of ~ 3.64 eV, leading to a thickness of > 1 μm. Besides, the data obtained from these analyses were used for cell performance analysis through the SCAPS 3.3 software-based simulation with a predicted power conversion efficiency of 23.59 %. It was observed that the PSC's short circuit current density and the thickness of the m-TiO₂ layer are inversely proportional, whereas the open-circuit voltage shows an independent effect on m-TiO₂ viscosity. This study envisages an initial trade-off between the m-TiO₂ layer's porosity, bandgap and thickness that can ensure the PSC with improved performance parameters.

1. Introduction

The photovoltaic performance of the PSC can be improved by enhancing the compositional engineering, especially the film morphology and thickness remains critical for stability and performance [1]. The viscosity of the solution or the concentration change in the precursor solution affects the film thickness and morphology [2]. This will directly lead to the variation in the PSC performance. The researchers investigated the influence of physical characteristics of different PSC layers while adding solvents with various rheological properties [3]. Shin et al. (2021) demonstrated the viscosity optimisation of perovskite by adding binary solvents and the effect of its rheological behaviour in increasing the lifetime and reducing the trap density for thicker perovskite films [3].

In a PSC, the perovskite layer is sandwiched between the hole and electron transport layer (ETL) and configuration changes with the cell structure [4]. Since the coating of each layer in the PSC is affected by the properties of the underneath layer, the rheological optimisation of all the solutions used in the PSC layer is essential. The ETL/perovskite

interface enhances the electron transport by inhibiting the carrier recombination and it improves the device performance [5]. Since the ETL layer controls the perovskite crystallisation, the electronic property and optical optimisations denoted the potential of bringing up high efficient PSC [6]. These includes energy mobility changes, transmittance and band gap modulations [6]. In this work, the traditional PSC configuration was studied to simulate its photovoltaic (PV) performance, where the experimental results of mesoporous-TiO₂ (m-TiO₂) were employed.

2. Materials preparations

The [supplementary information](#) (SI) explains all the material preparation details. Different m-TiO₂ pastes preparation method is mentioned in [Table S1](#) and the PV results generated using SCAPS 3.3 software-based simulation, and related details can be found in [Table S2](#).

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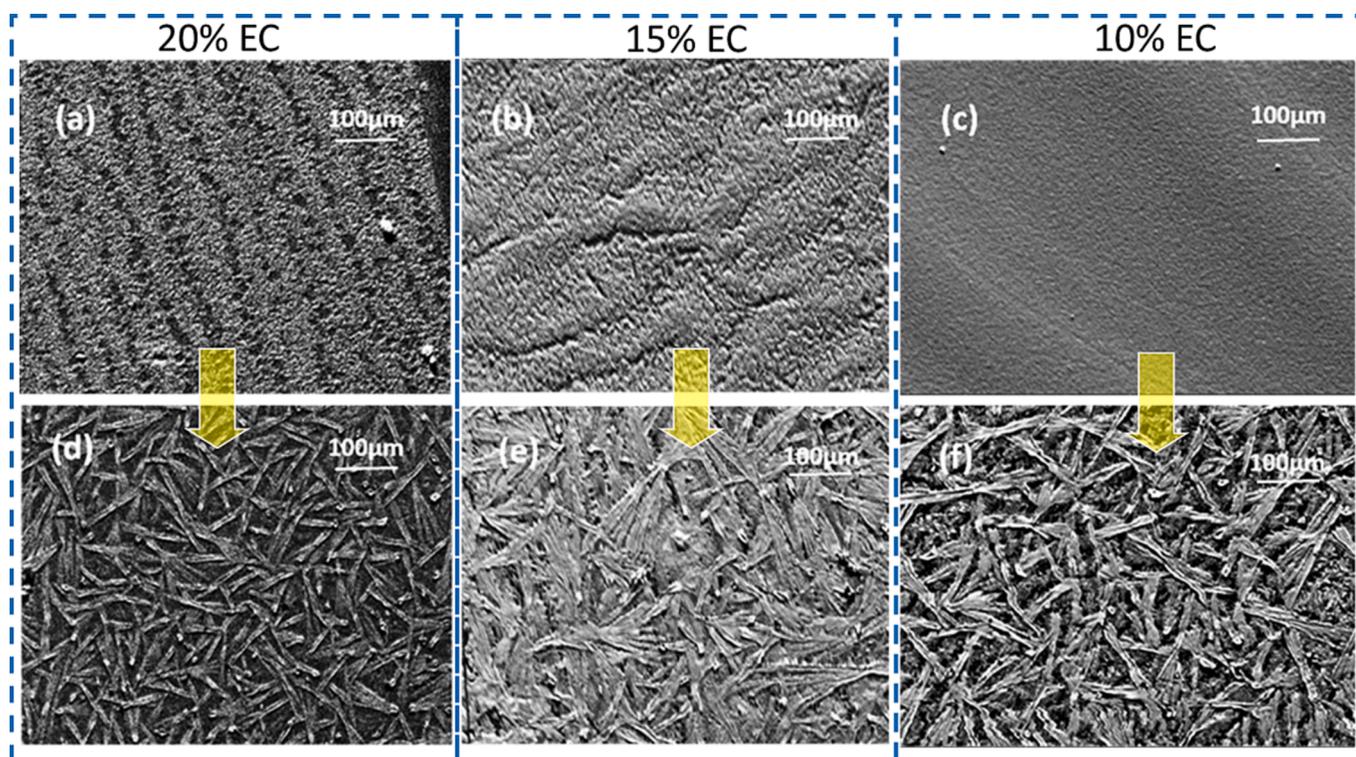


Fig. 1. SEM microstructural images of m-TiO₂ layers before and after coating perovskite; m-TiO₂ paste with (a) 20%, (b) 15%, (c) 10% of EC, respectively, and similarly corresponding MAPbI₃ coating for (d) 20%, (e) 15%, (f) 10% of EC, respectively.

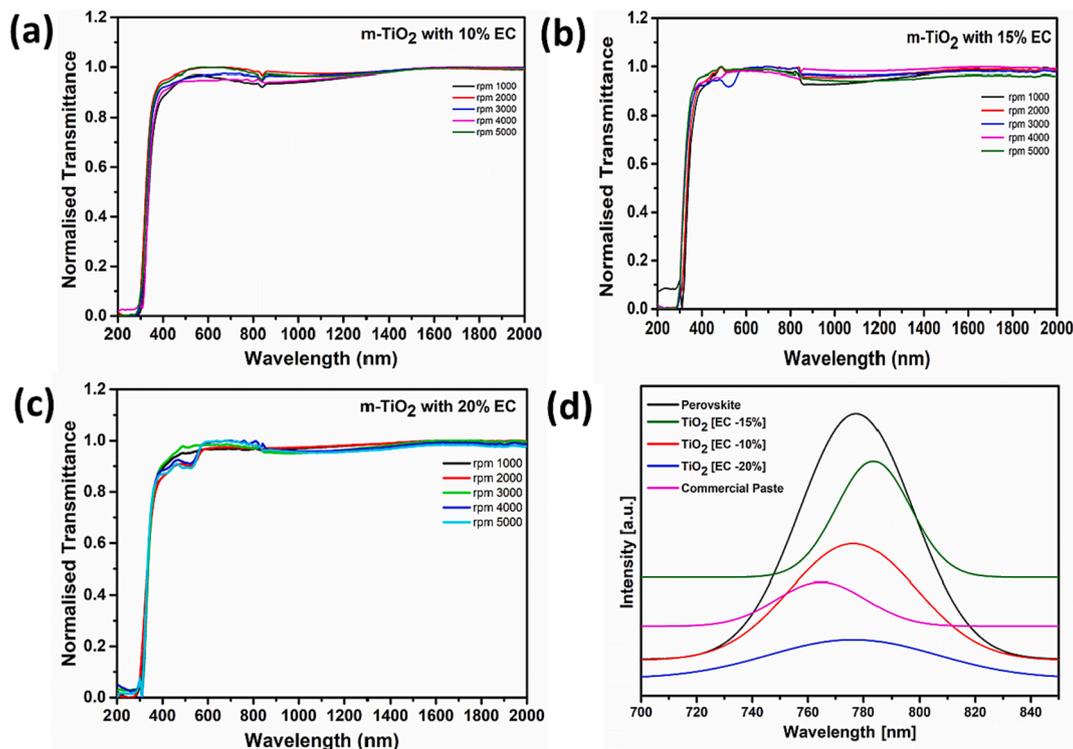


Fig. 2. Transmission spectra of the m-TiO₂ layer coated film at various rpm for (a) 10 %, (b) 15 %, (c) 30 % EC, respectively, and (d) PL spectra of various amounts of EC added m-TiO₂ with the perovskite films at an optimized 2000 rpm.

3. Experiment methods

The rheological and morphological behaviour of each paste were analysed after coating each of these pastes with different rpm, 1000,

2000, 3000, 4000 and 5000; and the absorbance and transmittance spectra were examined. The Tauc plot analysis showed the bandgap difference of different m-TiO₂ layers. The bandgap and thickness characteristics of each layer were simulated by using the SCAPS 3.3 software

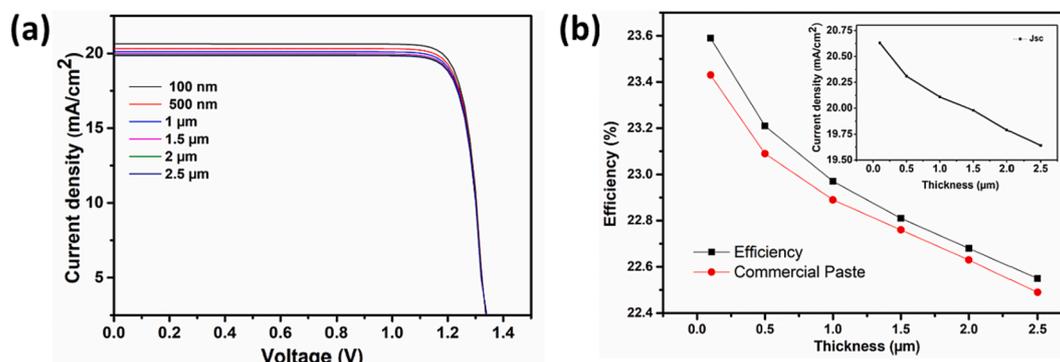


Fig. 3. Results from the SCAPS software simulation result (a) current–voltage characteristic plot of PSCs with different electron transport layer thicknesses and (b) efficiency–thickness and current–thickness plot of various PSCs.

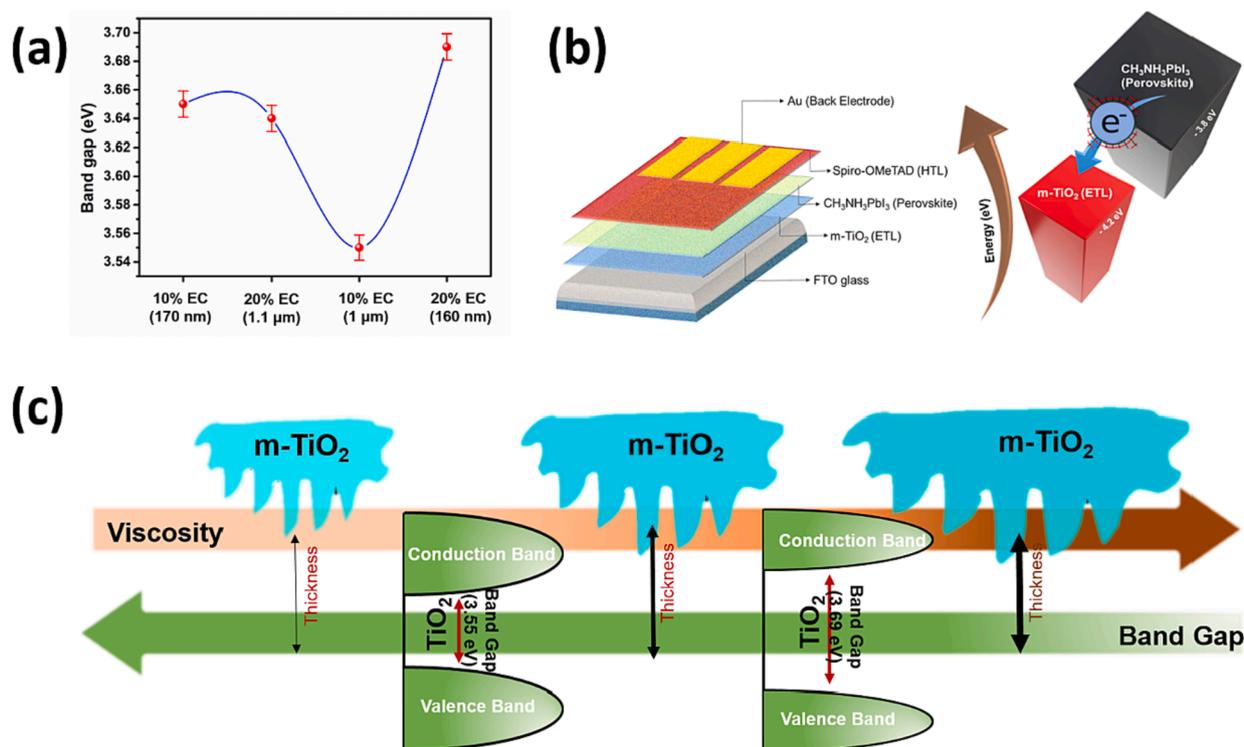


Fig. 4. (a) Band gap variation plot as a function of EC contained; a schematic representation of the (b) PSC configuration considered for the simulation study, and (c) the overall concept and observation of this study.

to study the PV performance. A detailed explanation included in SI.

4. Results and discussion

Considering that the $m\text{-TiO}_2$ layer plays an essential role in determining the perovskite film structure, uniformity and the porosity of the $m\text{-TiO}_2$ determine a crucial role in the PSC characteristics. While increasing the ethyl cellulose (EC) enhances the porosity of the $m\text{-TiO}_2$ films, as seen from the scanning electron microscopic (SEM) microstructure images Fig. 1a–c. Similarly, Fig. 1d–f exhibit the perovskite injected $m\text{-TiO}_2$ layers of the same films. SEM microstructures of the $m\text{-TiO}_2$ layers for different EC contents, where the distribution and homogeneity of the perovskite nanostructured turned out to have porous characteristics.

Fig. 2a–c represents the transmission spectra of the $m\text{-TiO}_2$ thin films deposited at different rpms. Almost all deposited films exhibited high transparency throughout the visible and infrared zones. However, Fig. 2b and c indicate that an optimum amount was required to achieve

maximum transparency, where higher EC-contained pastes are dominated by their visible absorption and slightly reduced transparency. Also, higher EC content can form inter-structural agglomeration, causing lesser transparency at the visible zone.

The PL spectra were measured at room temperature to analyse the efficiency of charge extraction from the perovskite to the $m\text{-TiO}_2$ layer and the recombination behaviours [7]. MAPbI_3 exhibits the broad emission, leading to a maximum wavelength of ~ 770 nm when excited at 530 nm (Fig. 2d) [8]. Depending on EC content, the thin films' PL peak intensity follows a trend of $20\% < 10\% < 15\%$. Greater homogeneity of the deposited perovskite layer on $m\text{-TiO}_2$ is believed to reduce the recombination of photo-induced charge carriers. To enhance the quality of the perovskite films, various strategies have been used, interface engineering, solvent and additive engineering are the most common ones [9].

Fig. 3a exhibits the simulated results of current density – voltage plots for varied $m\text{-TiO}_2$ thicknesses of the PSC devices. The simulation results signify an apparent current density (J_{sc}) decrement while

increasing the layer thickness, whereas the corresponding open-circuit voltage (V_{OC}) and fill factor emphasize insignificant changes. Usually, higher consistency of m-TiO₂ increases the charge transfer resistance, decreases the device's current density and affects the device's efficiency (Fig. 3b) [10].

Table S3, SI summarizes the results observed from the experimental and simulation study of the PSC device. The experimental results indicate viscosity variation of the m-TiO₂ paste and further layer's thickness by changing the rpm during its spin-coated fabrication. Fig. 4a describes band gap variation concerning different thickness samples. The band gap values calculated from the Tauc plot were further employed for simulation analysis. In this case, by keeping the m-TiO₂ layer's band gap value constant, the simulation results exhibit corresponding PV performance for different thicknesses (0.1–2.5 μm). The interrelation between the charge transfer and the thickness can be established concerning the m-TiO₂ layer's electrical conductivity [10]. The layer with 0.1 μm thickness has the lowest charge transfer resistance, so it displays a better current density and PCE. The rheological characterisation of the prepared pastes was done by varying the viscosity and fluid behaviour, and related details are available in Table S1, SI. As the Fig. S1 indicates the correlation between the shear rate and shear stress establishes a linear relationship. It and shows that the entire sample has a Newtonian behaviour or can be classified as a Newtonian fluid [10,11]. This agrees with the above relation and implies the quantum size effect operative in the present case. It is also known that a relatively large number of thin films and their density increase as the thickness increases to a particular thickness beyond which the density is practically constant. Fig. 4b represents a schematic form of the individual components for the PSC device and is considered for the simulation study. Besides, the effect of the m-TiO₂ layer's viscosity over thickness that affects the band gap of the m-TiO₂ layer and hence corresponding PV reference was schematically described in Fig. 4c.

5. Conclusion

Considering that m-TiO₂ is a crucial component of PSCs, we emphasize its impact on perovskite solar cell parameters in this work. In this work, it is evident that the rheological properties of the m-TiO₂ layer of the PSC have a critical effect on the current density of the PSC. In comparison, the viscosity changes in the m-TiO₂ layer show a difference in morphology, bandgap, and coating thickness. During m-TiO₂ coating's thickness increased from 0.1 μm to 2.5 μm , and the current density reduced from 20.63 mA/cm² to 19.64 mA/cm². Moreover, the efficiency decreased from 23.59 % to 22.55 % without altering its open-circuit voltage and fill factor. Because of the large-scale production of PSC, the fabrication technique's optimum thickness according to the fluid rheology characteristics are relevant. The large-scale controlled techniques like physical vapour deposition, ink-jet printing and slot-die coating methods have to be explored more with the PSC's ink rheology and the layer thickness.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matlet.2023.133960>.

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