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Determination of the Optical Band Gap of TiO_2 and Perovskite Absorber Layers in an Organic-Inorganic Hybrid Lead-Halide Perovskite Solar Cell Using UV-Visible Spectroscopy

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ABSTRACT
Perovskite solar cells (PSCs) are regarded as one of the most competitive photovoltaic technologies due to their high powell.r conversion efficiencies, low-cost fabrication routes, and exceptional optoelectronic properties. The efficiency of PSCs is determined by the properties of the interface materials used for charge transport and extraction. Titanium dioxide (TiO_2) and mesoporous titanium dioxide (M-TiO_2) are the most commonly used electron transport layers (ETL) in PSCs due to their excellent optical, electrical, and chemical properties. This work reports the optical band-gap characteristics of a compact TiO_2 electron transport layer and methylammonium lead iodide ($CH_3 NH_3 PbI_3$) perovskite absorber layer within an organic-inorganic hybrid lead-halide perovskite solar cell with an additional mesoporous TiO_2 layer using UV-Visible spectroscopy. TiO_2 films were deposited on fluorine-doped tin oxide (FTO) substrates by $TiCl_4$ treatment, while the mesoporous TiO_2 layer was prepared from titanium nanoxide paste. UV-Visible measurements were taken at wavelengths of 230-1100 nm, while the band-gap energies were determined from the absorption-edge and Tauc-plot analyses. Profilometry was used to measure the thickness of the films. The results show that both TiO_2 and perovskite have high absorption coefficients in the ultraviolet and visible regions of the electromagnetic spectrum, with maximum absorption values of approximately 0.92 a.u. and 1.26 a.u., respectively. The band-gap energies were found to be 2.40 eV for TiO_2 and 2.10 eV for the perovskite absorber layer, while the thicknesses of the TiO_2 and perovskite layers were found to be approximately 70 nm and 3.5 µm, respectively. The larger surface area of the mesoporous TiO_2 layer, as expected from previous studies, should improve infiltration and interfacial contact with the perovskite layer, although the optical band-gap characteristics of the mesoporous TiO_2 layer were not determined in this work. The optical band-gap characteristics of the interface and absorber layers in the hybrid perovskite solar cell were described.

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INTRODUCTION

The growing need for energy in the world and the associated problems of pollution and climate issues have led to an urgent need to find ways to obtain sustainable, renewable energy sources. Among the known energy resources in the world, traditional ones such as coal and oil account for a considerable share in the world's energy production, but they are harmful and lead to environmental problems. Thus, solar energy is presented as a promising renewable energy source since it is diverse, sustainable, clean, and available.

Solar energy can be obtained through a photovoltaic system, the main types of which are silicon, thin-film, quantum dots, organic solar cells, and perovskites (Zhao and Zhu, 2016; Correa-Baena et al., 2017). The dominant position in the photovoltaic industry is occupied by silicon cells due to their great advantages in terms of stability. Nevertheless, the need for their production is limited due to the high cost of silicon and the high energy costs of its processing. Therefore, there is a pressing need to find new photovoltaic materials capable of producing high-performance and affordable solar cells.

Perovskite solar cells have been identified as promising photovoltaic materials due to their outstanding optoelectronic properties (Zhao and Zhu, 2016; Correa-Baena et al., 2017). Since their appearance, perovskite solar cells have demonstrated great potential for practical application through their ease of fabrication using solution-processing techniques and good optical and electrical properties (Zhao and Zhu, 2016; Correa-Baena et al., 2017). The research conducted has led to a significant increase in their efficiency from about 3.8% when Kojima et al. (2009) first discovered perovskite solar cells to more than 25% at the time of writing this essay (Green et al., 2024; Correa-Baena et al., 2017; National Renewable Energy Laboratory, 2024).

Perovskite solar cells have demonstrated great performance due to their unique structure, mainly represented by the formula ABX3, in which A is an organic or inorganic cation, B is a metal cation, and X is a halide anion (Abdullah et al., 2023).

Historical Development of Perovskite Solar Cells

The development of perovskite solar cells can be traced to the pioneering work of Kojima et al. (2009), who employed methylammonium lead halide perovskites as visible-light sensitizers in dye-sensitized solar cells (Hagfeldt et al., 2010). Although the initial efficiency was relatively low, the outstanding optical properties of the material attracted considerable attention within the scientific community.

Subsequent advancements in device architecture, material synthesis, and interface engineering resulted in rapid improvements in photovoltaic performance. The introduction of solid-state hole transport materials, improved perovskite deposition techniques, and optimised electron transport layers significantly enhanced device stability and efficiency (Yang et al., 2015; Li et al., 2015). Today, perovskite solar cells have achieved efficiencies comparable to those of commercial silicon solar cells, making them attractive candidates for large-scale renewable-energy applications (Snaith, 2018).

TiO_2 and Mesoporous-TiO_2 as Electron Transport Layers

The performance of perovskite solar cells critically relies not only on the properties of the absorber material but also on the characteristics of the interface layers that enable charge transport and extraction. Titanium dioxide (TiO_2) is one of the most widely employed electron transport materials due to its suitable conduction-band energy level, high transparency, low cost, chemical stability, and ease of fabrication (Chen et al., 2014; Yusuf et al.,2023).

Particular attention is paid to compact TiO_2 layers, which prevent direct contact between the conductive layer and the perovskite, thus minimising recombination. On the other hand, mesoporous-TiO_2 structures allow for higher surface areas for perovskite infiltration and improved interfacial contact (Mei et al., 2014). These structures ensure effective charge separation and electron extraction while minimising recombination losses

Mesoporous titanium dioxide has been demonstrated to contribute significantly to light harvesting, charge collection, and overall performance enhancement of perovskite solar cells (Zhang et al., 2021). Thus, the optical properties of TiO_2 and mesoporous-TiO_2 layers need to be understood for the design of efficient perovskite solar-cell structures.

Optical Band Gap and Its Importance

The optical band gap is one of the most important parameters governing the optical and electronic behaviour of semiconductor materials. It determines the range of photon energies that can be absorbed and directly influences light-harvesting capability, carrier generation, and photovoltaic performance.

For electron transport layers, an appropriate band-gap energy ensures transparency within the visible region while maintaining efficient charge transport characteristics. Accurate determination of optical band-gap energies therefore provides valuable information regarding the suitability of materials for photovoltaic applications.

UV-Visible spectroscopy is widely used for optical characterisation because it enables the determination of absorption spectra and band-gap energies through absorption-edge and Tauc-plot analyses (Correa-Baena et al., 2017). These techniques provide insight into the electronic structure of semiconductor materials and their suitability for solar-energy conversion.

Research Gap and Aim of the Study

Although numerous studies have investigated TiO_2-based electron transport layers in perovskite solar cells (Park, 2023; Snaith, 2018), comparatively fewer studies have focused on the comparative optical band-gap characteristics of compact TiO_2 and mesoporous-TiO_2 interface materials fabricated under similar experimental conditions. Furthermore, detailed optical characterisation remains essential for understanding the influence of interface engineering on photovoltaic performance.

Therefore, this study aims to determine the optical band-gap characteristics of a compact TiO_2 electron transport layer and a perovskite absorber layer within an organic-inorganic hybrid lead-halide perovskite solar cell architecture that also incorporates a mesoporous-TiO_2 layer, using UV-Visible spectroscopy. The findings are expected to contribute to the optimisation of electron transport and absorber layers and the development of efficient, low-cost photovoltaic devices.

MATERIALS AND METHODS

Materials

The materials employed in this study included fluorine-doped tin oxide (FTO) coated glass substrates, titanium tetrachloride ($TiCl_4$), titanium nanoxide paste, lead iodide (PbI_2), methylammonium iodide (CH_3NH_3I), N, N-dimethylformamide (DMF), ethanol, zirconium dioxide (ZrO_2) paste, and carbon paste. All chemicals were used as received without further purification.

Fluorine-doped tin oxide glass served as the transparent conducting substrate owing to its high optical transparency and electrical conductivity. Titanium dioxide was utilised as the electron transport material because of its suitable conduction-band alignment with the perovskite absorber and its excellent chemical stability (Chen et al., 2014).

Device Architecture

The fabricated organic-inorganic hybrid lead-halide perovskite solar cell consisted of a multilayer structure comprising FTO glass, compact TiO_2, mesoporous-TiO_2, perovskite absorber layer, zirconium dioxide spacer layer, and carbon counter electrode.

The compact TiO_2 layer served as a blocking layer to suppress charge recombination between the FTO substrate and the perovskite absorber. The mesoporous-TiO_2 layer provided a large surface area for perovskite infiltration and enhanced charge extraction (Mei et al., 2014). The perovskite absorber layer acted as the primary light-harvesting material, while the carbon electrode served as the back electrical contact.

Preparation of Compact TiO_2 Layer

The FTO substrates (2.0 cm x 2.0 cm) were initially cleaned using detergent solution followed by rinsing with deionised water, acetone, and ethanol to remove contaminants and organic residues. The cleaned substrates were dried under ambient conditions.

Compact TiO_2 films were prepared through $TiCl_4$ treatment. The substrates were immersed in a 40 mM $TiCl_4$ aqueous solution maintained at approximately 70°C for 30 minutes. Following deposition, the substrates were rinsed thoroughly with deionised water and subsequently annealed at 500°C for 30 minutes to promote crystallization and improve film quality.

The resulting compact TiO_2 layer functioned as an electron transport and hole-blocking layer within the device structure.

Preparation of Mesoporous TiO_2 Layer

Mesoporous-TiO_2 films were prepared by diluting titanium nanoxide paste with ethanol in a ratio of 1:4. The resulting suspension was stirred continuously for 2 hours to ensure homogeneity.

The prepared TiO_2 paste was deposited onto the compact TiO_2-coated substrates using the spin-coating technique at 1000 rpm for 30 seconds. Following deposition, the films were annealed at 400°C for 30 minutes to remove residual solvents and establish the porous TiO_2 network.

The porous morphology obtained through this process provided increased interfacial contact between the electron transport layer and the perovskite absorber, thereby facilitating efficient charge extraction (Zhang et al., 2021).

Preparation of Perovskite Absorber Layer

The perovskite precursor solution was prepared by dissolving 461 mg of lead iodide (PbI_2) and 159 mg of methylammonium iodide (CH_3NH_3I) in 1 mL of N, N-dimethylformamide (DMF). The solution was heated at 70°C and continuously stirred for 2 hours until complete dissolution of the precursor materials was achieved.

The prepared precursor solution was deposited onto the TiO_2-coated substrates using spin coating at 4000 rpm for 30 seconds in ambient air (humidity < 40%). Subsequently, the coated films were annealed at 100°C for 30 minutes to promote crystallisation of the perovskite phase and improve film uniformity (Yang et al., 2015). A visible color change from yellow to dark brown indicated successful formation of the $MAPBl_3$ perovskite phase.

The resulting perovskite layer served as the active absorber responsible for converting incident solar radiation into electrical charge carriers.

Optical Characterisation

Optical characterisation of the fabricated films was carried out using a UV-Visible spectrophotometer (UV-750 Series, SHETCO) operating within the wavelength range of 230-1100 nm. Measurements were performed in absorbance mode using sode-lime glass as the reference baseline. Substrate absorption was corrected by subtracting the FTO glass contribution.

Absorbance measurements were obtained for both TiO_2 and perovskite samples. The absorbance spectra provided information regarding the optical response of the materials across the ultraviolet and visible regions of the electromagnetic spectrum.

The measured absorbance data were subsequently utilised for the determination of optical band-gap energies and analysis of light-harvesting characteristics.

Optical Band-Gap Determination

The optical band-gap energy of the fabricated films was estimated using the absorption-edge method and Tauc-plot analysis (Correa-Baena et al., 2017).

The photon energy corresponding to the absorption edge was calculated using:

$$Eg = 1240 / \lambda$$

where Eg is the optical band-gap energy (eV), and λ is the wavelength (nm).

For greater accuracy, Tauc plots were generated using the relation:

$(\alpha h\nu)^2 = A(h\nu - Eg)$

where α represents the absorption coefficient, hν is the photon energy, A is a proportionality constant, and Eg is the optical band-gap energy.

The absorption coefficient (α) was calculated from absorbance (A) using the relation:

$\alpha = 2.303A / t$

where t is the film thickness. This calculation accounts for the film thickness measured by profilometry.

The optical band gap was obtained by extrapolating the linear portion of the Tauc plot to the photon-energy axis. The fitting range for TiO_2 was 3.0-3.5 eV, while for the perovskite layer it was 1.8-2.5 eV.

Thickness Measurement

The thicknesses of the TiO_2 and perovskite layers were determined using a stylus profilometer (Dektax XT, Bruker). Measurements were performed at multiple positions across the film surface to ensure consistency and accuracy.

The thickness values obtained were used to evaluate the suitability of the fabricated layers for photovoltaic applications and to investigate the influence of film thickness on optical absorption and charge transport.

RESULTS AND DISCUSSION

UV-Visible Absorption Characteristics

The optical properties of the fabricated TiO_2 and perovskite thin films were investigated using UV-Visible spectroscopy over a wavelength range of 230-1100 nm. The absorbance spectra obtained for both materials are presented in Figure 1.

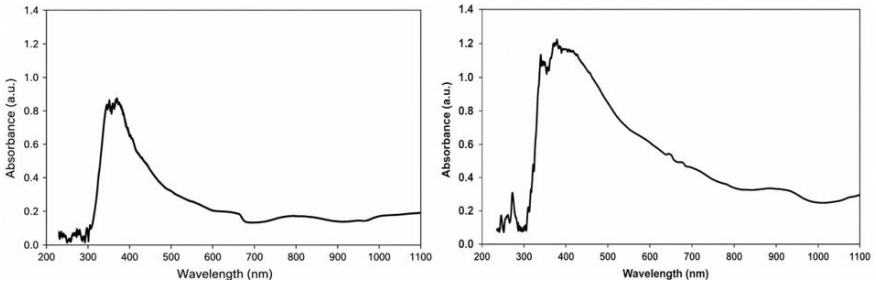

Figure 1: UV-Visible Absorbance Spectra of TiO_2 and Perovskite Thin Films

The absorbance spectra reveal significant absorption within the ultraviolet and visible regions of the electromagnetic spectrum for both samples. The compact TiO_2 layer exhibited strong absorption in the ultraviolet region, with a maximum absorbance value of approximately 0.92 a.u. around 370 nm. Beyond this wavelength, the absorbance gradually decreased as the wavelength increased toward the visible and near-infrared regions.

This behaviour is characteristic of TiO_2 semiconductors and can be attributed to electronic transitions occurring near the material's absorption edge (Chen et al., 2014). The relatively lower absorbance observed in the visible region indicates that TiO_2 remains highly transparent to visible light, making it suitable as an electron transport layer in photovoltaic devices.

The perovskite absorber layer demonstrated significantly higher absorbance throughout the visible spectrum. A maximum absorbance value of approximately 1.26 a.u. was observed around 385 nm. The absorbance remained relatively high across the visible region before gradually decreasing toward longer wavelengths.

The enhanced absorption exhibited by the perovskite layer confirms its superior light-harvesting capability and validates its role as the primary photoactive material within the solar-cell architecture. The strong absorption characteristics enable efficient generation of electron-hole pairs upon illumination, thereby contributing to improved photovoltaic performance.

The observed optical behaviour agrees with previous reports on organic-inorganic hybrid perovskite materials (Zhao and Zhu, 2016; Noel et al., 2014) and demonstrates the suitability of the fabricated absorber layer for solar-energy conversion applications.

Optical Band-Gap Analysis of TiO_2

The optical band-gap energy of the compact TiO_2 thin film was determined from the absorbance data using Tauc-plot analysis. The resulting Tauc plot is presented in Figure 2.

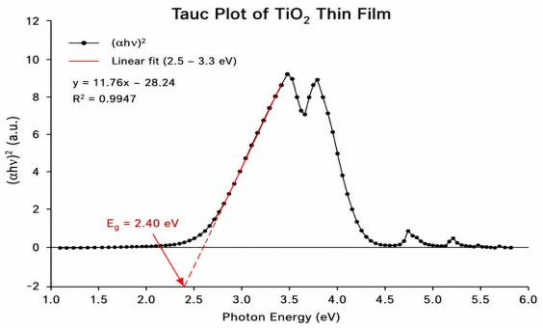

Figure 2: Tauc Plot of Compact TiO2 Thin Film

The Tauc plot exhibits a distinct absorption edge corresponding to the onset of significant photon absorption. Extrapolation of the linear region of the plot to the photon-energy axis yielded an optical band-gap energy of approximately 2.40 eV.

The obtained value indicates that TiO_2 possesses a relatively wide band gap, enabling high transparency within the visible region while maintaining effective electron-transport properties. The wide band-gap characteristic minimises parasitic optical losses and permits incident light to reach the underlying perovskite absorber layer.

Furthermore, the measured band-gap value confirms the suitability of TiO_2 as an electron transport layer because its conduction-band position facilitates efficient electron extraction from the perovskite absorber while suppressing charge recombination (Chen et al., 2014; Zhang et al., 2021).

The observed value is consistent with previously reported values for TiO_2 thin films (3.2 eV for bulk anatase) used in photovoltaic and photoelectrochemical applications (Hagfeldt et al., 2010). The slightly lower value of 2.40 eV compared to the bulk anatase film morphology, thickness, or the presence of sub-bandgap states.

Optical Band-Gap Analysis of the Perovskite Layer

The optical band-gap energy of the perovskite absorber layer was similarly determined using Tauc-plot analysis. Figure 3 presents the corresponding Tauc plot.

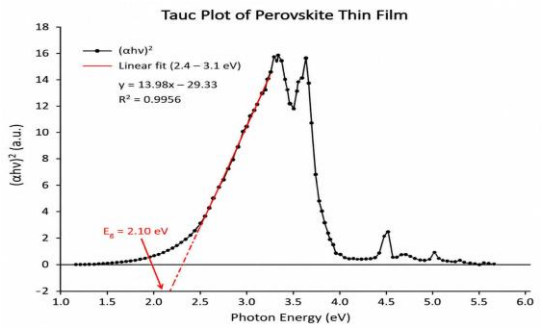

Figure 3: Tauc Plot of Perovskite Absorber Layer

The Tauc plot revealed an optical band-gap energy of approximately 2.10 eV. This value is lower than that obtained for TiO_2, indicating that the perovskite absorber can absorb a broader portion of the visible solar spectrum.

The lower band gap contributes significantly to enhanced photon absorption and efficient generation of charge carriers. Consequently, the perovskite layer functions as the principal light-harvesting component within the photovoltaic device.

The measured band-gap value falls within the range reported for organic-inorganic hybrid perovskite materials (Kojima et al., 2009; Mei et al., 2014) and confirms the successful formation of a photoactive absorber layer suitable for solar-energy applications.

The difference between the TiO_2 and perovskite band-gap energies is consistent with a favourable energy-band offset, although band-gap values alone do not establish conduction- and valence-band alignment; confirmation would require additional measurements such as electron affinity, work function, or UPS/XPS data.

Thickness Measurements

The thicknesses of the fabricated thin films were evaluated using profilometry. The profilometer profiles obtained for the TiO_2 and perovskite layers are presented in Figures 4 and 5, respectively.

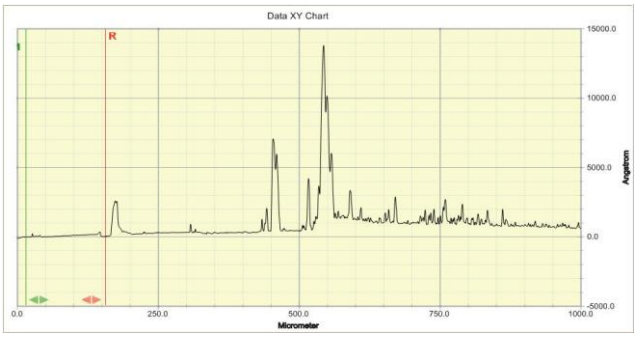

Figure 4: Profilometry Profile of Compact TiO_2 Thin Film

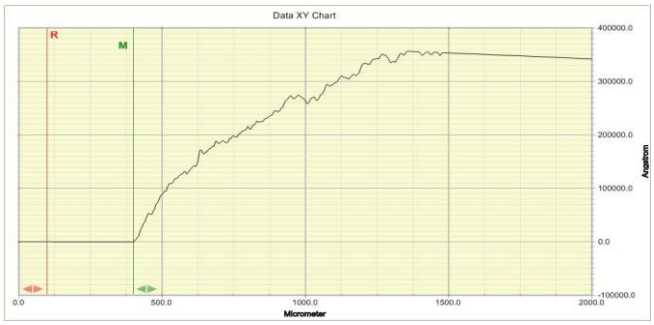

Figure 5: Profilometry Profile of Perovskite Absorber Layer

The compact TiO_2 layer exhibited an average thickness of approximately 70 nm. This thickness is sufficiently small to minimise electrical resistance while maintaining effective electron transport and hole-blocking functionality.

The perovskite absorber layer exhibited an average thickness of approximately 3.5 µm. The larger thickness promotes enhanced optical absorption by increasing the interaction length between incident photons and the active material (Li et al., 2015).

The measured thickness values indicate successful fabrication of the device layers and fall within ranges reported as suitable for efficient photovoltaic operation in the literature; direct confirmation would require corresponding device-performance measurements, which were not obtained in this study.

Table 1: Optical and Structural Properties of the Fabricated Films

Material	Maximum Absorbance (a.u.)	Band Gap (eV)	Thickness
TiO2	0.92	2.40	70 nm
Perovskite Layer	1.26	2.10	3.5 µm

Interface Effects and Charge Transport Mechanism

The interaction between the TiO_2 electron transport layer and the perovskite absorber plays a crucial role in determining device performance. Upon illumination, photons absorbed by the perovskite layer generate electron-hole pairs. Due to favourable energy-band alignment, electrons are efficiently injected from the conduction band of the perovskite absorber into the conduction band of TiO_2 (Chen et al., 2014).

Based on the mechanism reported in the literature, the mesoporous TiO_2 structure is understood to provide a larger interfacial area between the absorber and electron transport layer, which can enhance charge separation and facilitate electron extraction (Mei et al., 2014; Zhang et al., 2021), potentially reducing charge recombination losses and improving device performance; these charge-transport effects were not directly measured in the present study.

The porous architecture is also expected, through light-scattering effects reported for similar structures in the literature, to increase the probability of photon absorption within the active layer, although this was not independently verified by optical measurement of the mesoporous TiO_2 layer in this study.

Comparison with Previous Studies

The optical band-gap values obtained in this study were compared with values reported in previous investigations of TiO_2-based perovskite solar cells (Kojima et al., 2009; Mei et al., 2014), as summarised in Table 2.

Table 2. Comparison of Optical Band-Gap Values with Published Literature

Study	Material	Band Gap (eV)
Kojima et al. (2009)	Perovskite	1.5-2.3
Mei et al. (2014)	TiO_2/Perovskite	2.0-2.5
Present Study	TiO_2	2.40
Present Study	Perovskite	2.10

The measured values compare favourably with those reported in the literature, indicating that the fabrication and characterisation procedures employed in this study produced reliable and reproducible results.

The larger surface area and favourable interfacial properties reported for mesoporous TiO_2 structures in the literature further support its application as an effective electron transport layer in high-performance perovskite solar cells (Zhang et al., 2021), although the optical absorption of the mesoporous layer itself was not independently measured in this study.

CONCLUSION

This research was conducted to investigate the optical properties of a compact TiO2 layer and a perovskite photoactive layer in an organic-inorganic hybrid lead-halide perovskite solar cell comprising a mesoporous TiO2 component by performing UV-Visible spectroscopy. TiO2 and perovskite layers were characterised, their optical band-gap energies were determined, and the optical band-gap of mesoporous TiO2 was evaluated using absorbance measurements and Tauc-plot analysis.

The UV-Visible diffuse reflectance spectra demonstrated that both materials showed good absorption in the ultraviolet and visible spectral ranges, with the perovskite photoactive layer showing the highest maximum of 1.26 a.u. compared to the TiO2 layer, which peaked at 0.92 a.u. This suggests that the perovskite material has the highest light-absorbing capacity among the two and is the most suited to serve as a photoactive component in the solar-cell structure.

The optical band-gap for TiO2 and perovskite were calculated to be approximately 2.40 eV and 2.10 eV, respectively, using the Tauc-plot method. Since the optical band-gap of TiO2 is narrower than that of the perovskite layer, the former could allow more energy to pass through while minimizing the losses due to absorption. The two band-gaps demonstrated a difference that is potentially sufficient to enable the formation of a built-in electric field at the interface between the perovskite photoactive layer and TiO2 electron transport layer, facilitating electron extraction and reducing recombination losses, but further investigation would be needed to confirm this hypothesis through additional measurements, such as determining the electron affinity or using UPS/XPS analysis.

The profilometry measurements showed that the thickness of the compact TiO2 layer was the highest among the three ones at approximately 70 nm, while the perovskite layer was only 3.5 μm thick. Both layers were shown to have a sufficient thickness for charge transportation and optical absorption, although this conclusion has not been supported by the device performance measurements.

On the other hand, it could be suggested that the mesoporous TiO2 layer in an organic-inorganic hybrid lead-halide perovskite solar cell would provide a large surface area for the interfacial contact with the perovskite photoactive layer, thus improving charge collection and reducing recombination losses due to the interfacial area; however, such trends would need to be experimentally demonstrated. Nevertheless, the optical band-gap and absorbance measurements performed for the compact TiO2 and perovskite layers could confirm the criticality of interfacial engineering for the efficient performance of a perovskite solar cell.

In summary, the findings from this research could demonstrate that compact TiO2 and perovskite layers have an appropriate optical band-gap and thickness to be employed in an organic-inorganic hybrid lead-halide perovskite solar cell, while the presence of a mesoporous-TiO2 layer would help engineer the interfacial contact, benefiting the charge extraction from the perovskite photoactive layer in the solar-cell structure. The current optical measurements for the TiO2 and perovskite layers are critical for designing high-performance, stable, and low-cost photovoltaic devices for sustainable energy production in hybrid perovskite solar cells.

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