ABSTRACT: The electrically insulating space layer takes a fundamental role in monolithic carbon-graphite based perovskite solar cells (PSCs) and it has been established to prevent the charge recombination of electrons at the mp-TiO₂/carbon-graphite (CG) interface. Thick 1 μm printed layers are commonly used for this purpose in the established triple-mesoscopic structures to avoid ohmic shunts and to achieve a high open circuit voltage. In this work, we have developed a reproducible large-area procedure to replace this thick space layer with an ultra-thin dense 40 nm sputtered Al₂O₃ which acts as a highly electrically insulating layer preventing ohmic shunts. Herewith, transport limitations related so far to the hole diffusion path length inside the thick mesoporous space layer have been omitted by concept. This will pave the way toward the development of next generation double-mesoscopic carbon-graphite-based PSCs with highest efficiencies. Scanning electron microscope, energy dispersive X-ray analysis, and atomic force microscopy measurements show the presence of a fully oxidized sputtered Al₂O₃ layer forming a pseudo-porous covering of the underlying mesoporous layer. The thickness has been finely tuned to achieve both electrical isolation and optimal infiltration of the perovskite solution allowing full percolation and crystallization. Photo voltage decay, light-dependent, and time-dependent photoluminescence measurements showed that the optimal 40 nm thick Al₂O₃ not only prevents ohmic shunts but also efficiently reduces the charge recombination at the mp-TiO₂/CG interface and, at the same time, allows efficient hole diffusion through the perovskite crystals embedded in its pseudo-pores. Thus, a stable V_OC of 1 V using CH₃NH₃PbI₃ perovskite has been achieved under full sun AM 1.5 G with a stabilized device performance of 12.1%.

KEYWORDS: sputtering, Al₂O₃ space layer, interface recombination, perovskite solar cells, carbon-graphite, double-mesoscopic, HTM-free

INTRODUCTION

Perovskite solar cells (PSCs), a spin-off from dye-sensitized solar cells (DSSCs), have rapidly improved in achieving a very high power conversion efficiency (PCE) of around 25.2% since their first introduction in 2009. PSCs have a perovskite photoabsorber typically sandwiched between an electron transporting layer (ETL), and a hole transporting layer (HTL). Under illumination, photogenerated carriers are produced inside the perovskite absorber material. Ideally, electrons are extracted by the ETL acting as a photoanode and holes are transported from the perovskite through the HTL to the cathode. Spiro-OMeTAD is popularly used as the hole transporting layer in PSCs, albeit being highly expensive. Moreover, the commonly used gold electrode adds to higher manufacturing costs. To reduce the production costs, Spiro-OMeTAD and gold as a material were replaced in 2013 with a new architecture with carbon-graphite (CG) as the counter electrode with an initial 6.64% PCE. This architecture is...
known as the hole transport material (HTM)-free graphite-based PSCs and is one of the lowest-cost solar cell concepts with reduced manufacturing costs. Here graphite is not used as a HTL but as a direct contact material to the photo-generated holes in the perovskite. For this reason, the presence of an insulating material between the ETL and graphite electrode becomes crucial to avoid pure ohmic shunts. In this architecture, the selective layers and electrode are first processed through deposition techniques such as screen printing, while the infiltration of the perovskite active material is carried out as the last step through drop coating. Various multi-cation,
\textsuperscript{67} multi-halide,
\textsuperscript{8} and also lead-free perovskites,
\textsuperscript{10} are under research and implementation within this structure.\textsuperscript{11}

Even considering the recent promising advancements in long-term stability of PSCs,
\textsuperscript{11–13,6} the present degradation patterns have been attributed not only to the chemical decomposition of perovskite under thermal stress but also to the degradation of Spiro-OMeTAD. Long exposure to temperatures such as 85°C causes ion exchange between perovskite and Spiro-OMeTAD which results in the reduction of Spiro-OMeTAD,
\textsuperscript{14} leading to the decrease of hole conductivity and to the change in the perovskite crystal lattice.\textsuperscript{15} This problem is overcome in the HTM-free carbon-graphite-based PSCs (CG-PSC) thanks to the elimination of movable metal-ions (i.e., Au electrode) and dopants within the cell structure. It has been demonstrated that the CG-PSC is the most stable cell architecture with the longest device stability under various stress conditions.\textsuperscript{16,13,12}

Another advantage of CG-PSC is the ease of upscaling.\textsuperscript{17} In a recent report from Fu et al.,\textsuperscript{7} a non-certified efficiency of 10.09% at AM 1.5 G was achieved in a screen printed small area series interconnected module which had been encapsulated between two glasses using polyurethane hot melt lamination foil. The active area of this module was reported to be 60 cm\textsuperscript{2}. The modules were tested in outdoor conditions and showed promising stability for 2136 h although not continuously measured at the maximum power point.\textsuperscript{18} Also, 1 year stability has been reported for CG-PSCs with a 10 × 10 cm\textsuperscript{2} active area by Gracini et al.\textsuperscript{12} This type of architecture shows the potential for future commercialization of very low-cost PSCs.

As mentioned earlier, it is widely accepted in literature that a space layer (SL) is required in the HTM-free CG-PSCs to prevent the direct ohmic shunt pathways between the screen printed mesoporous TiO\textsubscript{2} (mp-TiO\textsubscript{2}) as the electron transport layer and the screen printed porous carbon-graphite as the conductive counter electrode. Thick 1 μm screen printed mesoporous ZrO\textsubscript{2} is widely used as an insulating layer. This architecture with three mesoporous layers (ETL, thick space layer, counter electrode) stacked on top of each other is popularly referred to as triple-mesoscopic PSCs. Liu et al. described the relevant parameters for an optimal space layer, such as its thickness, perovskite pore filling, morphology of perovskite within the pores, and uniformity of coating.\textsuperscript{19} Among all the parameters, the thickness of the space layer plays a pivotal role. It has been reported that thicknesses of over 1 μm affect the open-circuit voltage (V\textsubscript{OC}) and the fill factor (FF) due to the limited hole diffusion length and the charge recombination. Nevertheless, screen printed space layers with thicknesses lower than 1 μm impact the overall electrical parameters because of poor film quality and reduced light harvesting.\textsuperscript{19} Also, a different approach to the conventional screen printed pure mp-ZrO\textsubscript{2} space layer has been reported. Here a composite 1 μm space layer consisting of TiO\textsubscript{2} particles surrounded by 5 nm ZrO\textsubscript{2} particles has been used. A non-certified efficiency of 13.8% and a V\textsubscript{OC} of 935 mV have been shown by Liu et al.\textsuperscript{20} In 2018, we published a CG-PSC stabilized with screen printed mp-ZrO\textsubscript{2} as the insulating layer showing a V\textsubscript{OC} of 1 V through an innovative molten-salt approach attaining a certified and steady-state PCE of 12.6%.\textsuperscript{21} This is the highest certified stable V\textsubscript{OC} and efficiency reported so far in HTM-free triple-mesoscopic CG-PSCs with only mp-ZrO\textsubscript{2} as the insulating layer. This value points out that in the path toward V\textsubscript{OC} increase, a relevant contribution is due to as much as the quality of perovskite crystallization and its interconnecting ability to the charge extracting layers.\textsuperscript{22}

Al\textsubscript{2}O\textsubscript{3} is a famous material used for surface passivation and as a tunneling junction in microelectronics due to its wider bandgap (8.8 eV). Following this property, Al\textsubscript{2}O\textsubscript{3} has recently also been used as a space layer instead of ZrO\textsubscript{2}. Generally, 500 nm −1 μm thick mesoporous Al\textsubscript{2}O\textsubscript{3} layers have been deployed by printing. V\textsubscript{OC} = 893 mV has been achieved in such devices.\textsuperscript{22} A higher V\textsubscript{OC} of 1008 mV has been reported with the combination of printed Al\textsubscript{2}O\textsubscript{3} and NiO as the HTL layer.\textsuperscript{23} The combination of Al\textsubscript{2}O\textsubscript{3} and mp-ZrO\textsubscript{2} has also been reported for CG-PSCs. Xiong et al. showed the improvement in voltage through surface modification and space tuning by introducing a vacuum evaporated thermally oxidized 50 nm Al\textsubscript{2}O\textsubscript{3} as an interlayer between 1 μm mp-TiO\textsubscript{2} and 1 μm mp-ZrO\textsubscript{2} achieving V\textsubscript{OC} = 950 mV.\textsuperscript{24} Recently, ALD processed Al\textsubscript{2}O\textsubscript{3} has been fabricated as a passivation layer directly on top of the transparent conductive oxide (TCO) electrode layer.\textsuperscript{25} Here, a 5 nm thickness showed efficient tunneling of electrons, whereas 10 nm already resulted in an insulating behavior.

In this work, we present for the first time a cell architecture in which a thick mesoscopic space layer is avoided by using an ultra-thin sputtered Al\textsubscript{2}O\textsubscript{3} as insulator to prevent direct electrical contact between ETL and CG, giving rise to double-mesoscopic PSCs. Figure 1a shows the focused ion beam cut cross-sectional scanned electron microscope (FIB-SEM) image of this new device architecture prior to the filling

![Figure 1.](https://dx.doi.org/10.1021/acsanm.9b02563) ACS Appl. Nano Mater. 2020, 3, 2463–2471
of the perovskite, and the magnified cross-section of the mp-TiO2/Al2O3 interface is shown in Figure 1b. The energy level alignment of the material stack is depicted through the energy band diagram in Figure 1c.24,26,28 In this double-mesoscopic architecture, upon illumination photogenerated electron-hole pairs are created in the perovskite crystals (filled in mp-TiO2/Al2O3/Cs). Owing to the band energy alignment (as shown in Figure 1c), the electrons are injected into the mp-TiO2 and can be extracted by the outer terminals while, the holes diffuse through the perovskite to reach the CG counter electrode. The function of the thin insulating Al2O3 layer is therefore to prevent the electrical connection of electrons in the mp-TiO2 to the CG that creates direct shunt and recombination pathways. To differentiate from the widely used triple-mesoscopic architecture in literature (mesoporous ETL, thick mesoporous isolation layer, mesoporous counter electrode), hereafter we refer to our structure as double-mesoscopic PSCs (mesoporous ETL, sputtered thin isolation layer, mesoporous counter electrode).

A detailed description on sputtering parameters for the Al2O3 layer used and optimized for our devices is given in the Supporting Information (Note 1 and Figure S1). Pictorial representation showing the architectural difference of a triple-mesoscopic CG-PSCs compared to a double-mesoscopic CG-PSCs is shown in Figure S2. Results from optimizing the isolation layer thickness in the range between 10 and 100 nm shows that 40 nm already guarantees optimal performance of CG-PSCs, and we introduce the new double-mesoscopic CG-PSC architecture.

MATERIALS AND METHODS

Cell Fabrication. 100 × 100 mm² FTO TEC 7 glass plates were patterned using an argon laser to create both electrodes on a single glass to be used as monolithic cell. These plates were then cleaned in an ultrasonic bath containing 3% Deconex OP153 at 60 °C for 2 min and rinsed with DI water to remove the soap residues. Further they were ultrasonically treated in the bath for 1 min at 60 °C and rinsed with DI water to remove the soap residues. Further they were illuminated from the glass side for the purpose of photoinitiating the mp-TiO2 particles. UV-LED (Omnicure LX400) emitting a wavelength of 365 nm which provides maximum power of 320 mW was used. The cell was placed at a distance of 10 cm from the UV-LED source such that the entire active area of 0.4 cm² was illuminated. The J-V curves were measured using a potentiostat (Ivium CompactStat) between −2 and 2 V with a slow scan rate of 5 mV/s.

Characteristics and Stabilized Measurements. To obtain the I-V characteristics, the cells were illuminated using a Class A xenon arc lamp (Wacom, 1000W) solar simulator, the intensity of which was set according to a reference Si solar cell calibrated by Fraunhofer ISE Callab. The temperature of the measurement chuck and measurement table was maintained at 25 °C using a circulating cooling mechanism. Also a cooling fan was used to dissipate the heat from the top surface of the device. I-V values were measured using a potentiostat (Ivium CompactStat). The cells were covered with an active area mask of 0.4 cm² to prevent the influence of non-active illuminated areas. The cells were light soaked for 1 min before measuring the voltage at open circuit for 100 s. This stable voltage measurement was followed by measuring the reverse J-V scan from 1.1 V to −0.1 V and the forward J-V scan from −0.1 to 1.1 V at a scan rate of 50 mV/s. The voltage at maximum power point (Vmp) was obtained from the reverse scan, and the corresponding stable PCE for 200 s was observed at that selected Vmp.

VOC Decay Measurements. For the cells presented in this report, the secondary carriers were measured for 45 s and 60 s. The cells were illuminated using a red LED (635 nm) from Thorlabs. The cells were light soaked to keep the same condition carried out during the I-V measurement. The light was switched off and the resulting voltage decay curve was captured using a PicoScope 5000 series in case for 40 ms and Ivium CompactStat for 60 s measurement. The measurement was carried out in a dark room to prevent the influence of stray light.
Light-Intensity Dependent Measurements. The LED array from Ivium CompactStat was used to illuminate the cell at different intensities. The intensity was tracked in terms of klux (conversion factor used is 143 klux = 1 sun). At each set of intensities, the voltage was stabilized at open circuit for 60 s and was plotted against their corresponding sun intensity (log scale).

Time-Dependent Photoluminescence Measurement. The cells were placed under an optical microscope and were illuminated using a red LED (635 nm) from Thorlabs, of which the 2 mm spot diameter was resulting in an intensity of approximately 1 sun. The voltage and the current were monitored using Ivium CompactStat (with a integration time of 0.2 s) while the photoluminescence signal (with an integration time of 0.5 s) was simultaneously acquired using an Andor scMOS camera. The image was processed using Andor software.

RESULTS AND DISCUSSION

Characterization of Sputtered Pseudo-porous Al2O3 Isolation Layer. With the aim of achieving ultra-thin and conformal covering for the fabrication of an insulation layer in carbon-graphite based perovskite solar cells (CG-PSCs) and of choosing a manufacturing technique that can allow the transition to larger scale production, in this report we chose sputtered Al2O3 as the isolating layer in CG-PSCs. Many literature reports show that the layers achieved using the sputtering technique is compact in nature.27–29 However, in this section, we show that the compactness for a very thin layer is governed by the underlying layer onto which they are sputtered. To study this difference, the morphology of a sputtered layer on a flat substrate and on a mesoscopic layer was examined. Figure 2 shows the top-view scanned electron microscope (SEM) image of 10 nm Al2O3 sputtered on top of the Si substrate (Figure 2a) and on mp-TiO2 (Figure 2b).

Their corresponding atomic force microscopy (AFM) images are shown in Figure 2c,d. Both SEM and AFM reveal that the Al2O3 sputtered on a mesoporous layer is less dense mirroring/adapting to the morphology of the underlying mp-TiO2 layer. Thus, as observed, a pseudo-porous layer is formed when a compact layer adapts to the porosity of the underlying porous layer. The change in the morphology of the sputtered layer facilitates the infiltration of perovskite precursor solution that is drop casted as the last step in the CG-PSCs production.

The crystalline property of the sputtered Al2O3 was investigated through transmission electron microscope (TEM) and X-ray diffraction in grazing incidence mode (GIXRD). The TEM image in Figure 2e shows the lattice of the TiO2 nanocrystals (as parallel lines) indicating the presence of the crystalline TiO2 layer. A non-defined layer surrounding the parallel lines defines the presence of an amorphous Al2O3. Additional information showing the elemental presence of Al is shown in Figure S3a. Further measurements with GIXRD in Figure S3b confirm the presence of the amorphous nature of the sputtered Al2O3.

Interesting to note is that this thin and conformal covering layer is enough to isolate the TiO2 nanoparticle from the electrical contact with the flaky nature of the carbon-graphite electrode.

With the aim to optimize the Al2O3 layer, four different thicknesses (10 nm, 20 nm, 40 nm, and 100 nm) have been sputtered atop 1.5 μm of the mesoporous TiO2 (mp-TiO2). As a reference, a sample without Al2O3 was compared and is hereafter referred to as w/o SL (without space layer). Figures S4 and S5 illustrate the importance of Al2O3 sintering for achieving a surface modification through an increase in the particle size leading to thicker particle boundaries.30 We noted that sintered layers further reduce the surface tension owing to improvement of solution percolation.31,32

SEM images of the different Al2O3 thicknesses (with exception of 20 nm) on mp-TiO2 in tilted and cross-sectional view are shown in Figure 3. The porosity of the mp-TiO2 layer is noticeable in the SEM of the layer stack without Al2O3 (w/o SL) (Figure 3a). Additionally, it is clearly visible in Figure 3b–d that the sputtering leads to the formation of an Al2O3 layer with high open porosity at 10 nm and nearly closed particle boundaries at 100 nm as a result of the dense Al2O3 structure growth. It is important to allow complete infiltration and homogeneous crystallization of the perovskite solution in the cell stack. This ensures efficient light-harvesting and efficient charge transfer thanks to the electrical coupling of perovskite crystals with the cathode. Therefore, it is expected that the Al2O3 thickness increase will hinder infiltration of the perovskite precursor solution to fill the underlying mesoporous layer and thereby result in lower photocurrent. To have a better insight on the percolation ability through the pseudo-porous Al2O3 layer, wetting properties of different Al2O3 thicknesses on mp-TiO2 were analyzed through contact angle (CA) measurements. Detailed information on CA measurements can be found in the Supporting Information, Figure S6.

Characterization of Double-Mesoscopic CG-PSC Prior to Perovskite Infiltration. The concept of double-mesoscopic CG-PSC cell architecture allows the complete fabrication of a mesoporous device structure prior to the perovskite infiltration which occurs as the final step (the processing technique of all layers in the cell architecture is...
explained in detail under the methods section. Therefore, we were able to analyze the electrical isolation over the mp-TiO2/CG interface as a function of the thickness of the isolation layer independent of the interaction with perovskite. For this purpose, the mp-TiO2 layer itself had to be made conductive by direct photoexcitation over the bandgap of TiO2 (3.2 eV) using UV light. The mechanism of conduction has been recently explained by Stevanovic et al. originating from the result of an electron density gradient.33

Figure 3. Tilted SEM images of different Al2O3 thicknesses sputtered on 1.5 μm of mp-TiO2 (a) No Al2O3, referred as w/o SL; (b) 10 nm Al2O3; (c) 40 nm Al2O3; and (d) 100 nm Al2O3. Corresponding cross-sectional images are seen in the inset. (b) Al2O3 10 nm thick, forms a uniform particle spread monolayer on top of the mp-TiO2 layer providing a pseudo-porous pathway for solution infiltration. The images show the increase in the particle size and layer compactness with increasing Al2O3 thickness.

Figure 4. Shunt detection by analyzing the perovskite independent UV-induced photocurrent at the mp-TiO2/CG interface. The current voltage characteristics (J–V) curve of unfilled CG-PSCs (c-TiO2/mp-TiO2/Al2O3/CG) with varying thickness of Al2O3, illuminated under UV-LED (365 nm) is plotted. With increasing thickness of the Al2O3 a strong isolation effect is observed as can be seen from the very low currents (<1 μA/cm2) at a forward voltage larger than 1.0 V. The unshunted complete cells are shown in Figure 5. A defined presence of Al2O3 on top of mp-TiO2 is noticed along with a good pore filling of the mp-TiO2 with the perovskite showing that thin Al2O3 layers have not hindered the percolation of the precursor solution.

The results from stabilized photovoltage measurements of the complete cells are shown in Figure 6a. By just adding a very thin 10 nm Al2O3 to the mp-TiO2/CG interface, already a 130 mV increase in photovoltage was observed. On further optimization, we reached stabilized 1 V for devices with 40 nm Al2O3.

VOC vs light intensities of Figure 6b gives additional information on the nature of shunts and the diode ideality factor present in the cells under investigation. This is referred to as suns-VOC measurement. All five samples show a linear behavior in a logarithmic plot even at low sun intensities indicating the absence of ohmic shunts. The type of recombination present in the devices is known by calculating the ideality factor n using eq 1.35

\[
n = \frac{\epsilon}{k_B T} \left( \frac{dV_{OC}}{d \ln(I_{1mW/cm^2})} \right)
\]

where \( \epsilon \) is the charge on an electron \( \epsilon = 1.602 \times 10^{-19} \) C, \( k_B \) is the Boltzmann’s constant \( k_B = 1.38 \times 10^{-23} \) J K\(^{-1}\), and \( T \) is temperature in kelvin (K). In literature it has been reported that the \( n \) value of PSCs varies with the \( V_{OC} \) stabilization time.36 This also agrees with our measurements. To illustrate this effect, Figure 8 shows the suns-\( V_{OC} \) measurement for devices without Al2O3 at two time intervals, namely 0 s (\( V_{OC} \) unstabilized) and 60 s (\( V_{OC} \) stabilized over 60 s). The voltage to determine the points of lowest current at the respective photovoltage. Linear-scale J–V curves of the same measurements and the scheme of the experimental setup are shown in Figure S7. For Al2O3 thicknesses above 40 nm, the current density over the space charge region at the mp-TiO2/CG interface at \( V_{OC} \) is only in the range of a few nano amperes as a result of pin-hole free and an efficient isolating layer. Therefore, a high barrier potential against electron transfer to the CG counter electrode larger than 1.3 V is observed for an Al2O3 thickness more than 40 nm which is similar in value to the theoretically achievable photovoltage of 1.34 V for the CH3NH3PbI3 (MAPI) perovskite absorber34 to be applied later in the full device.

Characterization of Perovskite-Filled Complete Device. Focused ion beam-scanned electron microscopy (FIB-SEM) image and energy dispersive X-ray (EDX) analysis of a perovskite filled double-mesoscopic HTM-free CG-PSCs are shown in Figure 5. A defined presence of Al2O3 on top of mp-TiO2 is noticed along with a good pore filling of the mp-TiO2 with the perovskite showing that thin Al2O3 layers have not hindered the percolation of the precursor solution.

The EDX elemental mapping of Al shows the clear and definite presence of Al2O3 on top of mp-TiO2. Pb EDX mapping further shows that the mesoporous layers are well filled with perovskite crystals.
Figure 6. All measurements include complete perovskite-filled devices with c-TiO2/mp-TiO2/Al2O3/CG with different thicknesses of Al2O3. (a) Stabilizing V_OC measured for 100 s at 1000 W/m² AM 1.5 G; (b) V_OC decay measured at various sun intensities under an LED array; (c) V_OC decay measurement for 45 ms with cells illuminated using red LED as the light source with a constant current of 5650 mA (approximately 1 sun intensity); (d) V_OC decay measurement for 60 s with cells illuminated using red LED as the light source with a constant current of 5650 mA (approximately 1 sun intensity).

Comparison shows high n value (1.36) for unstabilized V_OC (at 0 s) due to overestimation of the dominant order recombination. Only stabilized V_OC values (after 60 s) have been considered for Figure 6b.

In an ideal solar cell, charge recombination occurs between the conduction band and the valence band. This recombination is often referred to as bimolecular recombination leading to an ideality factor of \( n = 1 \). On the opposite, recombination solely from occupied trap states results in a higher ideality factor of \( 2 (n = 2) \). In real solar cells both recombination types co-exist resulting in an ideality factor between 1 and 2. It has also been reported in the literature that mesoscopic perovskite solar cells have an ideality factor of \( \sim 1.5 \).

Devices without Al2O3 show the n value of 0.92 pointing to a situation with unoccupied traps. The observation of the low photovoltage of 750 mV at 1 sun indicates that there is low density of photoexcited charges present in the perovskite. This leads us to the conclusion that electrons from the conduction band of the TiO2 are pulled away by the carbon-graphite substrate leading to a strong and fast emptying of shallow trap states in the mp-TiO2. However, with the increase in Al2O3 thickness, the electrons in the mp-TiO2 become now well isolated from the CG. This means that traps are now occupied, leading toward an \( n = 2 \) type recombination behavior. At the same time, the charge carrier density in the conduction band of the mp-TiO2 and the perovskite is high, leading to a high photovoltage. A similar observation has also been recently reported and interpreted by Tress et al. The pictorial representation of the recombination pathway mechanisms and its corresponding n factor is shown in Figure S9.

Under open circuit conditions, the external photo current in a solar cell is zero by definition. This means that the photovoltage is determined by the equilibrium between the photogenerated charges and the charge recombination. Open circuit voltage decay (OCVD) measurements provide there-

fore information on the charge carrier recombination in the bulk. Initial decay at high photovoltage is determined by the fast recombination of the primary charge carriers followed by the slower non-radiative recombination of charges from shallow traps and deep traps at lower voltages. The graphs in Figure 6c,d show the decay from the stabilized V_OC of our cells under illumination after the light is switched off. The sharp decrease in the V_OC decay as soon as the illumination is switched off is caused by the fast recombining primary charge carriers and the recombination from shallow traps. In the time frame of seconds (Figure 6d), the voltage value is determined by the very slowly recombining secondary charges (i.e., deep trapped charges in mp-TiO2). The upward shift in the voltage with respect to increasing Al2O3 thickness up to 40 nm shows that the thin isolation layer efficiently prevents the recombination of electrons at the mp-TiO2/CG interface. Thus, the impact of fast recombination at the interface (mp-TiO2/CG) is reduced by introducing Al2O3 of 40 nm (or thicker) resulting in higher photovoltages and long-living charges. Interestingly, the voltage decay even for devices without Al2O3 is slow in the seconds range. This indicates that the decay from the deep traps is negligible in all cases and shows the absence of ohmic shunts. The absence of ohmic shunts has been studied in more detail for the case of devices without Al2O3. An external 1 kΩ resistor was connected in parallel for the voltage decay measurements. As shown in Figure S10 the voltage drops to zero in less than 50 µs demonstrating the absence of an internal ohmic shunt. The observation of the fast decay (i.e small amount of trapped charge) also validates the mechanism of emptying the shallow traps through the mp-TiO2/CG interface as described in the previous section.

In general, photoluminescence (PL) in solar cells results from radiative recombination between the electrons in the conduction band and the holes in the valence band. It is therefore a direct measure of the density of photoexcited primary charge carriers. In open circuit conditions, the PL is only limited by the internal recombination, whereas under short circuit conditions the electrons are drawn out leading in an ideal case to a full quenching of the PL. The intensity of PL quenching (i.e., the comparison between PL_{V_OC} and PL_{V_SC}) is therefore a reciprocal measure of the current contributed by the primary charge carriers. Moreover, it is limited by the charge transport and the concentration of electrons in non-radiative traps (i.e., secondary charges). Measuring the PL quenching is a good method to check the charge transport in perovskite solar cells.

Voltage, current, and averaged PL signal as derived from time-dependent PL imaging were recorded under constant illumination when the devices were switched between open circuit (OC) and short circuit (SC) conditions. The graph in Figure 7a shows the corresponding results for devices from the same batch with 10 nm Al2O3, 40 nm Al2O3, 100 nm Al2O3, and without Al2O3 (w/o SL). The quenching in PL intensity and the increase in current while switching from V_OC to V = 0 V (short-circuit condition) shows the charge extraction ability of the devices. We observe at least a double exponential behavior in quenching of the PL intensity for the devices with Al2O3, which stabilize at the same low values after 20 s. This behavior corresponds to efficient non-limited charge transport. This is confirmed by the high J_{SC} values of these devices (as reported later). The PL images corresponding to the 9th s and the 30th s are compared in Figure 7b, which evidently shows...
The efficient and uniform PL quenching in the monitored area in devices with Al₂O₃. In contrast, devices without Al₂O₃, after switching to SC conditions, show an initial fast quenching of the average PL followed by slow recovery of the PL toward the initial value under OC conditions (V_OC) and short circuit condition (V = 0 V). The measurements were carried out using a red LED as the light source with a constant current of 1413 mA, of which the 2 mm spot diameter resulted in an intensity of approximately 1 sun. (b) PL images of all devices at the 9th and 30th s (i.e., stabilized in open circuit and in short circuit conditions) which show an efficient and improved charge extraction for devices with Al₂O₃ with maximum voltage, current, and PL quenching observed in devices with 40 nm Al₂O₃ as the insulation layer.

Figure 7. Differentiating between primary charge carrier transport by observing space resolved photoluminescence (PL) after switching from open circuit conditions to short circuit conditions both at constant illumination. Measurement on filled devices with c-TiO₂/mp-TiO₂/Al₂O₃/CG with different thicknesses of Al₂O₃. (a) The graph shows the voltage, current, and PL measured while switching between two conditions, namely open circuit condition (V_OC) and short circuit condition (V = 0 V). The measurements were carried out using a red LED as the light source with a constant current of 1413 mA, of which the 2 mm spot diameter resulted in an intensity of approximately 1 sun. (b) PL images of all devices at the 9th and 30th s (i.e., stabilized in open circuit and in short circuit conditions) which show an efficient and improved charge extraction for devices with Al₂O₃ with maximum voltage, current, and PL quenching observed in devices with 40 nm Al₂O₃ as the insulation layer.

Figure 8. Stabilized PCE measurement of champion device (c-TiO₂/1.5 μm mp-TiO₂/40 nm Al₂O₃/CG) achieving stable 12.1% PCE.

J–V curves of the best devices from each condition are presented in Figure S12a. As shown in Figure 8, a stable PCE of 12.1% for the champion device was measured with a masked area of 0.0876 cm². Its corresponding J–V curve is shown in Figure S12b. Furthermore, the histogram shown in Figure S12c,d depicts the reproducibility of double-mesoscopic devices.

Hence, as a proof of concept we point out that progress is made in this article by converting the triple-mesoporous structure to the double-mesoporous architecture with a significant increase in the open circuit voltage. A successful replacement of the thick spacer layer (ZrO₂ or Al₂O₃) with an ultra-thin isolation layer provides a reduction of the transport limitations of such PSC architecture. Thus, our results show the capability and true potential of double-mesoscopic HTM-free CG-PSCs and bring to the conclusion that the state-of-the-art thick space layers limit the performance of CG-PSCs.

**CONCLUSION**

In this work, a new double-mesoscopic architecture has been introduced for hole conductor (HTM)-free carbon-graphite (CG) perovskite solar cells (PSCs) favoring more efficient charge transport compared to existing triple-mesoscopic CG-PSCs. We could show that a thin 40 nm sputtered pseudo-porous Al₂O₃ layer can compensate the need of a conventional micrometer thick (>1 μm) mesoporous insulating space layer in triple-mesoscopic CG-PSCs. By concept, this allows a smaller diffusion length for holes inside the perovskite photoabsorber. With this new configuration, a high photovoltage of 1.0 V and a stabilized solar efficiency of 12.1% have been reached for CH₃NH₃PbI₃ (MAPI) perovskites which already outperforms the results reported for high temperature processed triple-mesoscopic CG-PSCs using standard MAPI perovskite by others.

SEM, EDX, and AFM measurements show that the fully oxidized sputtered Al₂O₃ layer covers the underlying mesoporous TiO₂ (mp-TiO₂) layer. The pseudo-porosity of Al₂O₃ is therefore governed by the roughness of the underlying layer. The Al₂O₃ thicknesses have been finely tuned between 10 and 100 nm for an optimal infiltration of the perovskite solution and allow full perovskite crystallization inside the mp-TiO₂ electrode layer. The absence of pure ohmic shunts in the presence of Al₂O₃ has been shown prior to the infiltration of perovskite using direct photoexcitation of the TiO₂ layer with UV. Light-dependent photovoltage and photovoltage decay as well as time-dependent photoluminescence measurements
showed that the optimal 40 nm thick Al2O3 efficiently reduces the charge recombination at the mp-TiO2/CG interface and, at the same time, allows efficient hole diffusion through the perovskite crystals embedded in its pseudo-pores.

The outcome of our report opens the discussion that an ultra-thin space layer efficiently isolates the CG counter electrode from electrons which have been transferred from the perovskite to the mp-TiO2. The thickness of the isolation layer has been optimized to achieve a high stable Voc by preventing the interfacial recombination of free electrons from the illuminated perovskite region at the CG interface.

**ASSOCIATED CONTENT**

1. **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsanm.9b02563.

Investigation on the Al2O3 layer influenced by sintering: information on its wetting properties (through contact angle measurement), material consistency (through line EDX, SEM, GIXRD and AFM) and the device performance statistics; average electrical parameters; J–V curves of the best devices (PDF)

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Author Contributions
G.M. planned and performed the experiments and wrote the main part of the paper. A.H. proposed the concept idea of the work. S.B. and T.K. carried out sputtering experiments. L.W. and D.B. contributed with valuable discussions and L.W. also with the idea for TiO2 photoaivation through UV. S.M. and A.H. revised the manuscript.

**Funding**

G.M. acknowledges the scholarship support from Stage Graduate Funding program of Baden-Württemberg (LFGF). L.W. and D.B. acknowledges the scholarship support of German Federal Environment Foundation (DBU). S.M. gratefully acknowledges the funding by the Project PROPER financed from the German Federal Ministry of Education and Research under the funding No. 01DR19007. We acknowledge the project UNIQUE, supported under the umbrella of SOLAR-ERA.NET_Cofund by ANR, PtJ, MIUR, MINESCO-AEI, SWEA. SOLAR-ERA.NET is supported by the European Commission within the EU Framework Programme for Research and Innovation HORIZON 2020 (Cofund ERA-NET Action, No. 691664). This project has received funding from the European Union’s Horizon 2020 research and innovation program under Grant Agreement No.763989 (APOLO). This publication reflects only the author’s views and the European Union is not liable for any use that may be made of the information contained therein.

**ACKNOWLEDGMENTS**

The authors thank J. Zielonka for carrying out SEM/EDX measurements, B. Krishna Das for sputtering, K. Eble for the 3D drawings, D. Martineau from Solaronix for helping in technical suggestion and device fabrication and C. Bouillet from Université de Strasbourg for TEM measurements.

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