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Graphene-engineered automated sprayed mesoscopic structure for perovskite device scaling-up.

Babak Taheri¹, Narges Yaghoobi Nia¹, Antonio Agresti¹,*, Sara Pescetelli¹, Claudio Ciceroni¹, Antonio Esaù Del Rio Castillo², Lucio Cinà³, Sebastiano Bellani², Francesco Bonaccorso²,⁴*, Aldo Di Carlo¹,⁵*

¹ CHOSE - Centre for Hybrid and Organic Solar Energy, Department of Electronic Engineering, University of Rome Tor Vergata, via del Politecnico 1, 00133, Rome, Italy;
² Graphene Labs, Istituto Italiano di Tecnologia, via Morego 30, 16163 Genoa, Italy
³ CICCI RESEARCH S.R.L., Grosseto (Italy)
⁴ BeDimensional Srl., Via Albisola 121, 16163 Genova, Italy
⁵ Department of semiconductor electronics and device physics, National University of Science and Technology “MISiS”, Leninskii pr.4, Moscow 119049, Russia

Abstract

One of the most thrilling developments in the photovoltaic field over recent years has been the use of organic-inorganic lead halide perovskite, such as CH₃NH₃PbI₃ (MAPbI₃), as a promising new material for low-cost and highly efficient solar cells. Despite the impressive power conversion efficiency (PCE) exceeding 22% demonstrated on lab-scale devices, large-area material deposition procedures and automatized device fabrication protocols are still challenging to achieve high-throughput serial manufacturing of modules and panels. In this work, we demonstrate that spray coating is an effective technique for the production of mesoscopic small- and large-area perovskite solar cells (PSCs). In particular, we report a sprayed graphene-doped mesoporous TiO₂ (mTiO₂) scaffold for mesoscopic PSCs. By successfully combining the spray coating technique with the insertion of graphene additive into the sprayed mTiO₂ scaffold, a uniform deposition and a significant enhancement of the electron transport/injection at the mTiO₂/perovskite electrode is achieved. The use of graphene flakes on the sprayed scaffold boosts the PCE of small-area cells up to 17.5% that corresponds to an increase of more than 15% compared to standard cells. For large-area (1.1 cm²) cells, a PCE up to 14.96% is achieved. Moreover, graphene-doped mTiO₂ layer enhances the stability of the PSCs compared to standard devices. The feasibility of PSC fabrication by spray coating deposition of the mesoporous film on large-area 21×24 cm² provides a viable and low-cost route to scale up the manufacturing of low-cost, stable and high-efficiency PSCs.

Keywords: Automated Spray Coating, Perovskite Solar Cell, Graphene, mesoporous TiO₂, interface engineering
1. Introduction

The power conversion efficiency (PCE) of solution-processed solar cells underwent a rapid progress, especially in the case of the organic-inorganic hybrid perovskite solar cells (PSCs), showing a record high PCE value of 22.7% in 2017 [1]. A prototypical PSC architecture comprises an organometal halide perovskite-based light-harvesting layer, sandwiched between a hole-transporting layer (HTL) and an electron-transporting layer (ETL). [2, 3] In particular, for the so-called mesoscopic structure, a mesoporous TiO$_2$ (mTiO$_2$) ETL is usually deposited onto a compact TiO$_2$ (cTiO$_2$) hole-blocking layer as photoelectrode (PE) scaffold. The mTiO$_2$ layer has a dual role consisting in both extracting the photo-generated electrons from the perovskite layer and transporting the charge towards the transparent conductive oxide (TCO) [2, 3]. The mesoporous scaffold structure accelerates the charge separation and the electron injection from the perovskite to the ETL [4], which allows the most efficient [5] and stable [6] PSCs to be fabricated. The photovoltaic performance achieved by PSCs with mesoscopic TiO$_2$ architectures (PCE > 20%) [7, 8] is encouraging the scientific community to scale up this technology. The possibility to fabricate large-area mesoscopic PSCs has already been proved in our recent work on graphene-based modules by adopting spin coating-based manufacturing. However, in this case, the module dimension is limited by the spin coater dimensions, which restricts the module active area to a few tens of cm$^2$ [9, 10]. Alternative deposition techniques, such as screen printing [11], blade coating [12], spray coating [13] and electrospray coating [14, 15], have been considered with efficiency on small area cells of 9.3%, 9.7%, 16% and 15%, respectively. However, their applicability to large-area format compatible with the controlled deposition of uniform mTiO$_2$ films is still an open issue [15].

Differently from a wet film deposition (typical of spin and blade coating, as well as screen printing techniques), during spray coating of mTiO$_2$ films, small droplets of material are deposited onto the substrate [16]. Consequently, spray coating is not affected by the roughness of the underlying layer or by the substrate pattern [17] and it can be applied on irregular surfaces with high reproducibility [18]. Moreover, it allows the whole device area to be covered in a second timespan without any restriction in terms of dimensions and geometry. Lastly, the possibility to spray any solution independently by the mixed precursors or doping materials makes the spray coating advisable to speed up and scale up the perovskite modules fabrication [13, 19] for their market entry [20-22]. Based on these considerations, Huang et al. [13] demonstrated superior charge transport properties for sprayed mTiO$_2$ nanoparticles compared to the corresponding spin-coated film, allowing PSCs to reach PCE higher than 16%. Moreover, PCE above 15% has been recently demonstrated for small-area PSCs based on electrospray-coated mTiO$_2$ as PE scaffold [15]. Despite these advances, the application of spray coating techniques to large-area PSCs is still limited to few cases [23-25], and the all-sprayed devices achieved PCEs which are still far (<11.7%) from the state-of-the-art [1]. Recently, both PCE and the stability of PSCs have been improved by exploiting 2D materials, e.g., graphene or MoS$_2$, to control the interface properties between the different layers in the PSC architecture [9, 10]. The advantage of this strategy, named as “Graphene Interface Engineering” (GIE), is linked with the possibility to
create and design layered artificial structures with on-demand electrochemical properties [26-30] by means of scalable, cost-effective and solution-processed methods [31-36]. In fact, the possibility to produce 2D materials from the exfoliation of their bulk counterparts in suitable liquids [37-43] enables functional inks to be formulated [44-47]. Subsequently, 2D material inks can be deposited on different substrates by well-established printing/coating techniques [48-53].

Based on the aforementioned considerations, graphene-based hole-blocking layer (or ETL) have demonstrated to reduce the energy barriers for electron collection at the PE, improving the short-circuit current density (JSC) [54-56]. For example, graphene/metal oxide composites improved the JSC of 23% compared to the one of graphene-free counterpart [54]. Graphene quantum dots (GQDs) and a lithium neutralized graphene oxide (GO-Li) have been used as interlayers between mTiO2 and perovskite absorber in a mesoscopic PSCs [55, 56] to accelerate the electron injection. Consequently, GQDs-based PSCs exhibit faster electron extraction time (90-106 ps) if compared with the PSCs without GQD (260-307 ps), while the use of GO-Li improved the linear trend of JSC-PSC curves with respect to that expressed by the reference cells.

Additionally, graphene has also been used to dope the mTiO2 [57, 58]. Actually, the presence of graphene into mTiO2-based ETLs reduced the interfacial resistance and improved the electron collection efficiency at the PE by demonstrating around a two-fold faster electron diffusion coefficient than the native ETL [57]. In particular, graphene-doped mTiO2 (Gr-mTiO2) layer deposited by spin coating has shown a record PCE above 16% and also improved stability, retaining more than 88% of the initial performance over 16 h of prolonged 1 SUN illumination at maximum power point (MPP) [58]. Actually, it is well-established that GIE is also an effective tool for the fabrication of efficient and durable PSCs [59].

Herein, we report the use of the GIE in order to fabricate PSCs via Automated Spray Coating (ASC) technique. The ASC enables Gr-mTiO2 to be deposited compatibly with high-throughput serial manufacturing of PSCs. The optimization of sprayed mTiO2 is assessed by studying its morphological, structural and electronic properties as a function of the substrate temperature and the concentration of mTiO2 paste. The sprayed Gr-mTiO2 paste allows PSCs to reach a PCE of 17.5 % and 14.96 % on 0.1 cm² and 1.1 cm² active areas, respectively. The use of graphene enables the PSC efficiency to be improved more than 16% compared to the reference device. Finally, electro-optical analysis exhaustively points out the role of graphene in the electron injection, trap states and charge transporting into the PE. Lastly, we show that the use of graphene into the mTiO2 partially mitigates the degradation phenomenon at perovskite/ETL interface, thus increasing the PSCs time life under operative conditions.

Methods

Graphene ink preparation

Liquid phase exfoliation of graphite flakes [60] (Sigma–Aldrich) in N-methyl-2-pyrrolidone (NMP) and subsequent solvent exchange process [61] were used to prepare graphene flakes ink in ethanol (EtOH, Sigma–Aldrich, + 99.8 %) at a concentration of 0.9 mg mL⁻¹. Experimentally, 3g of graphite flakes were dispersed in 300 mL of NMP and ultrasonicated for 6h. The obtained dispersion was then ultra-centrifuged at 16 000 g (in a Beckman Coulter Optima™ XE-90 with a SW32Ti rotor) for 30 min at 15 °C, exploiting sedimentation-based separation to remove thick flakes and un-exfoliated graphite. After the ultracentrifugation process, 80% of the supernatant was collected by pipetting. The pipetted sample was dried using a rotary evaporator at 70 °C, 5 mbar, then 500 mL of EtOH were added to the dried samples. The sample was then dispersed using a sonic bath for 10 min. Subsequently, the samples were centrifuged at 800 g (in a Beckman Coulter Optima™ XE-90 with a SW32Ti rotor). Then, the sediments were collected while the supernatant was discarded. This process of decantation was repeated twice, with the objective to wash out the NMP residuals. Finally, the sediments were dispersed in 200 mL of EtOH.

Solar cells fabrication

The solar cells were fabricated on Glass/FTO substrates, which were washed for 10 min with acetone, deionized water and EtOH, in an ultrasonic bath, consecutively. A TiO2 dispersion for spray pyrolysis deposition of cTiO2 consisted of 0.16 M diisopropylammonium acetylactonate (TiAcAc) and 0.4 M acetylacetonate (AcAc) in EtOH. The final thickness was 50 nm of the spray pyrolysis at 450 °C onto the pre-cleaned laser patterned FTO glass. For mTiO2 film deposition, anatase TiO2 nanoparticles paste (18NR-T, Dyesol) was used. The mTiO2 paste was dissolved into EtOH via stirring and ultrasonic bath to obtain 1.4 M, 1.6 M, 1.7 M and 1.8 M concentrations. Mesoscopic TiO2 films based on aforementioned concentrations were deposited by ASC technique. Then 0.4 M of TiAcAc was added to the mTiO2 dispersion, which was stirred for 1h. Then, the obtained dispersion was doped with graphene flakes dispersion in EtOH (concentration of 0.5%, 1% and 2% v/v were tested). The mTiO2 was then deposited onto the FTO/compact TiO2 substrates through ASC using setting deposition parameters reported in Table S1. For reference spin-coated mTiO2-based devices, TiO2 paste (18NR-T, Dyesol) was diluted with EtOH, (w/v ratio of 1:5), and spin-coated onto the cTiO2 surface at 1500 rpm for 20 s. The formed mTiO2 films were sintered at 480°C for 30 min using a previously reported protocol [62]. The CH3NH3PbI3 absorber layer was deposited by a previously reported crystal engineering method in...
atmospheric condition [62]. Briefly, 535 mg of PbI2 powder was dissolved in 1 ml DMF and spin-coated at 6000 rpm for 10 s, while the temperature of the solution was set to 70 °C, on the surface of the preheated (70 °C) mTiO2 film. Subsequently, the devices were annealed at 40 °C for 2 min (temperature raise time = 1 min) and at 60 °C for 1 min (temperature raise time = 1 min). In the second step, the cooled PbI2 layers were dipped in a solution of methylammonium iodide (CH3NH3I in anhydrous 2-propanol 10 mg mL-1) for 10 min at room temperature while the solution was kept under mechanical stirring during the dipping time. Then, the devices were washed immediately by spin coating 2-propanol with an acceleration rate of 6000 rpm for 10 sec. Finally, the devices were heated at 70 °C for 2 min (temperature raise time = 1 min), and at 115 °C for 4 min (temperature raise time = 3 min) with relative humidity of about 40% on a hotplate. After heat treatment, 100 μl of spiro-OMeTAD (73.5 mg ml-1) in chlorobenzene (CB) solution doped with 26 μl of tet-butylpyridine (TBP), 16.6 μl of Lithium Bis (Trifluoromethanesulfonyl) Imide (Li-TFSI) of stock solution (520 mg in 1 ml acetonitrile), and 7.2 μl of cobalt (II) complex solution (FK209 from Lumtec) was deposited as HTL by spin coating at 2000 rpm for 20 s. Finally, 80 nm of Au was deposited as counter electrode by thermal evaporation.

**Characterization**

Masked devices were tested by acquiring I-V curves under a Class A solar simulator (ABET Sun 2000) at AM1.5 and 100 mW cm-2 illumination conditions calibrated with a reference silicon cell (RERA Solutions RR-1002), using a Keithley 2420 as a source-meter in ambient condition without sealing. Sun simulator spectrum and class were measured with a BLACK-Comet UV-VIS Spectrometer.

The atomic force microscopy (AFM) analysis of the surface of the TiO2 thin films realized by spray and spin coating, was performed through an A.P.E. Research Atomic Force Microscope. Measurements were performed in non-contact mode with a silicon tip with a radius of 8 nm, mounted on a cantilever (resonance frequency=325 kHz) with a spring constant of 40 N m⁻¹.

Dark I–V, transient photovoltage (TPV), stability stress test at the MPP, and illumination intensity dependence of the Voc and Jsc were performed with a high speed four channel source meter. A white LED array (4200 Kelvin) tuneable up to 200 mWcm⁻² of optical power density-based measurement system.
(Arkeo-Cicci research s.r.l.) was used as light source. A spring contact-based sample holder was used to improve the repeatability of the experiments. Incident power conversion efficiency (IPCE) spectra were acquired by using a homemade setup.

Electrochemical measurements were performed in dark conditions at room temperature using an Auto-lab 302N Modular Potentiostat from Metrohm in the two-electrode configuration with a bias voltage ranging from 0.6 to 1 V. The sinewave perturbation used was 10 mV of amplitude with frequencies from 1 MHz to 1 Hz. The surface morphology of mesoporous layers and cross-section image were obtained by using Scanning Electron Microscope (SEM) FE-SEM ZEISS.

Results and Discussion

In mesoscopic PSCs, the light enters from the PE to excite the photoactive layer. Therefore, the light passes through the mTiO2 layer before reaching the perovskite over-layer. For this reason, the control of optical transparency, thickness, and roughness of the TiO2 film are crucial to achieve efficient PSCs [63, 64].

The morphological and optoelectronic properties of the final sprayed mTiO2 layer depend by several deposition parameters, i.e., the substrate temperature, the number of spray cycles, the distance between the spray nozzle and the substrate, the nozzle aperture, the air pressure, and, lastly, the distance between two adjacent spray lines (StepX), [65, 66] (see Figure 1a).

As a first step in the deposition optimization of the ASC process, we studied the influence of the substrate (FTO) temperature on the roughness and transparency of the resultant mTiO2 layer. Spin coating deposition of mTiO2 was also considered for comparison. Spray coating of commercial mTiO2 nanoparticles (18NRT) dispersed in EtOH (1:5 w/w ratio) was accomplished on the substrate heated at different temperatures (30 °C, 80 °C and 120 °C). As shown in Figure 1b-c, the highest substrate temperature (120 °C) resulted in a rough mTiO2 surface (> 80 nm), which caused a decrease of the average electrode transmittance (81.4%) with respect to that obtained for the other temperatures (83% for mTiO2 obtained by spray at 30°C and spin coating). On the other hand, the low substrate temperatures (30 and 80 °C) allowed the solvent to reach the substrate surface with a consequent flattening of the mTiO2 surface. Notably, the RMS roughness of the layer was also influenced by the overlap of two adjacent spray lines. The mTiO2 film deposited by using a distance between two adjacent spray lines of 14 mm (StepX = 14 mm) had the best width overlay of each sprayed spot (5 mm), since it results in lower roughness (28 nm) with respect to other StepX values. Atomic force microscopy topographies (Figure 1d) show that the sample realized by ASC had a root means square (RMS) roughness (22.4 nm) comparable to that of the spin-coated samples (21.3 nm) (see also Table S2).

The mTiO2 film morphology obtained for the deposition at 30 °C enabled the PSCs performance to be enhanced compared to that of the PSCs produced with higher temperatures, i.e., 80, 100 and 120°C (Figure 2a). More in detail, the PCE decreased by almost 60% and 80% when the substrate temperature for the mTiO2 spray coating increased from 30 to 80 °C and 120 °C, respectively. However, it is noteworthy that the highest PCE obtained for sprayed mTiO2-based PSCs (13.92%) was still 34% lower than that of reference PSCs produced by spin coating mTiO2 (15.69%).

In order to optimize the sprayed mTiO2 layer morphology, different concentrations of TiO2 dispersion (1.4 M, 1.6 M, 1.7 M and 1.8 M) were employed and titanium disopropoxide bis acetylacetonate (TiAcAc) was added to the sprayed dispersion.
Table 1. PSCs $V_{oc}$, $J_{sc}$, FF and PCE values for three different mTiO$_2$ dispersion concentrations with about 180 nm of sprayed mTiO$_2$ thickness, compared with those of standard spin-coated mTiO$_2$-based cells. Deposition have been performed with 30°C of substrate temperature and with StepX of 14 nm.

<table>
<thead>
<tr>
<th>Cell Type</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>$J_{sc}$ form integrated IPCE (mA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2 Spray coating 1.4M</td>
<td>0.871</td>
<td>-15.88</td>
<td>66.34</td>
<td>9.18</td>
<td>-14.95</td>
</tr>
<tr>
<td>(nzzle AP=8, P=1.5 bar)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spray coating 1.6M without TiAcAc</td>
<td>0.857</td>
<td>-15.41</td>
<td>65.80</td>
<td>8.69</td>
<td>-14.67</td>
</tr>
<tr>
<td>(nzzle AP=9, P=1.5 bar)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B1 Spray coating 1.6M</td>
<td>0.873</td>
<td>-16.60</td>
<td>66.10</td>
<td>9.58</td>
<td>-16.09</td>
</tr>
<tr>
<td>(nzzle AP=9, P=1.5 bar)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D1 Spray coating 1.8M</td>
<td>1.021</td>
<td>-19.77</td>
<td>68.94</td>
<td>13.92</td>
<td>-19.40</td>
</tr>
<tr>
<td>(nzzle AP=9, P=1.5 bar)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Standard Spin coating</td>
<td>1.018</td>
<td>-21.16</td>
<td>72.82</td>
<td>15.89</td>
<td>-20.65</td>
</tr>
</tbody>
</table>

Table 1. PSCs $V_{oc}$, $J_{sc}$, FF and PCE values for three different mTiO$_2$ dispersion concentrations with about 180 nm of sprayed mTiO$_2$ thickness, compared with those of standard spin-coated mTiO$_2$-based cells. Deposition have been performed with 30°C of substrate temperature and with StepX of 14 nm.

to improve the connectivity between the mTiO$_2$ nanoparticles [13] (details about the analysed concentrations are reported in the methods section). By adjusting spray parameter settings, (Table S1), the mTiO$_2$ film with thicknesses ranging from 150 to 200 nm [5, 67, 68] exhibited the lowest RMS roughness values (about 22 nm) (Figure S1). Therefore, small-area (0.1 cm$^2$) PSCs were produced with a mTiO$_2$ film thicknesses of 180 nm, as shown by a representative cross-sectional SEM image (Figure S2). The as-prepared cells without TiAcAc resulted in maximum PCE of 9.1%. The addition of TiAcAc into mTiO$_2$ dispersion resulted in a cell PCE improvement of +10% (Table 1). Notably, the highest average PCE of 13.92% was achieved for the PSCs produced by using a mTiO$_2$ concentration of 1.8 M. As shown in Figure 2b, the PCE enhancement was a consequence of the higher current density ($J_{sc}$) (-19.77 mA cm$^{-2}$) and Fill Factor (FF) (69%) compared with those of the PSCs fabricated with other mTiO$_2$ dispersion concentrations (1.4 M, 1.6 M and 1.7 M). We assign these effects to an effective crystallization of the perovskite into the 22 nm-rough mTiO$_2$, which help to reduce the carrier recombination and improve carrier transport and collection abilities [69-71].

The pore size for efficient infiltration of the perovskite into the mTiO$_2$ (Error! Reference source not found.) leads to the highest electron mobility and the lowest disorder in the interface with perovskite.

Although the sprayed mTiO$_2$-based PSCs achieved PCE of ~14%, their $J_{sc}$ and FF were still 10% lower than those of spin-coated mTiO$_2$-based PSCs (Table 1), suggesting that the electron recombination at mTiO$_2$/perovskite interface significantly affected the cell performance for sprayed mTiO$_2$ based devices compared to that of spin-coated mTiO$_2$-based ones [72, 73].

With the aim to further improve the physical and electrical sprayed mTiO$_2$ film.

With the aim to boost further the performance of the PSCs obtained by ASC the mTiO$_2$ dispersion was enriched with graphene flakes, resulting in hybrid mesoscopic films herein namedGr-mTiO$_2$). Graphene flakes were produced by the LPE [44], in NMP. The synthetic procedure is detailed in [58] and summarized in the Experimental section. Three different concentrations of graphene flakes dispersion (0.5%,1% and 2% v/v) were tested by fabricating PSCs with area of 0.1 cm$^2$. In agreement with the SEM images of the mTiO$_2$ surface morphology (Figure S3), the Gr-mTiO$_2$ films did not show any difference with respect to the pristine mTiO$_2$ films. Moreover, the films deposited by spray and spin coating have shown the same surface morphology with an average mTiO$_2$ particle size of ~21 nm.

In term of photovoltaic performance of the PSCs, the optimum concentration of graphene inside mTiO$_2$ was 1% v/v, which results in an increase of $J_{sc}$ and PCE of 13% and 23%, respectively, with respect to those of graphene-free reference (Figure S4). This means that a concentration of 1% v/v of graphene dispersion concentration into mTiO$_2$ dispersion can suppress the electron recombination, i.e., to increase the $J_{sc}$. However, once graphene concentration exceeded 1% v/v, the PSC performance decreased. This trend can be ascribed to the increase of Gr-mTiO$_2$ light absorption by increasing graphene flakes concentration that strongly affects the optical transmittance of the PE (see Figure S5) [74]. This effect is also observed in the performance of graphene-based cells, in which $J_{sc}$ begins to decrease beyond the optimum graphene loading of 1% v/v (see Figure S4a).

Perovskite solar cells with and without graphene and for both spray and spin coating of mTiO$_2$ were fabricated and compared. To deposit mTiO$_2$ by ASC, the optimized graphene dispersion with a concentration of 1% v/v of was incorporated into the 1.8 M mTiO$_2$ dispersion. In order to demonstrate the uniformity of large-area mTiO$_2$ obtained by ASC, firstly the spray coating was accomplished on a large-area substrate (24x20 cm$^2$). Secondly, the substrate was divided into 2.5x2.5 cm$^2$ pieces, subsequently selected from different areas of the initial substrate, to finalize the fabrication of entire PSCs. On these substrates, devices were made with different active areas 0.1 cm$^2$ and 1.1 cm$^2$ (herein named small- and large-area
PSCs, respectively) by using the deposition parameter settings previously optimized (see Methods section for details).

**Figure 3** reports the electrical parameters (PCE, $J_{sc}$, FF and $V_{oc}$) for PSCs based on pristine mTiO$_2$ and Gr-mTiO$_2$ deposited by ACS and spin coating techniques. Notably, for both deposition techniques, the Gr-mTiO$_2$ led to a significant enhancement of $J_{sc}$ with respect to pristine mTiO$_2$. In particular, for small-area cells (0.1 cm$^2$), the spray-deposited Gr-mTiO$_2$ led to a ~16% increase of $J_{sc}$ with respect to the mTiO$_2$-based PSCs, whereas the graphene doping for spin-coated mTiO$_2$ improved the $J_{sc}$ of 5% with respect to the graphene-free reference.

The average PCE of spray Gr-mTiO$_2$ based devices was 16.8%, *i.e.*, higher than the spin-coated mTiO$_2$-based PSCs (15.6%). For pristine sprayed mTiO$_2$-based PSC, the average

<table>
<thead>
<tr>
<th>Type of cells</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spray Pristine mTiO$_2$</td>
<td>1.063</td>
<td>-18.571</td>
<td>66.712</td>
<td>13.165</td>
</tr>
<tr>
<td></td>
<td>(1.05±0.012)</td>
<td>(-18.91±0.46)</td>
<td>(65.15±2.14)</td>
<td>(12.94±0.26)</td>
</tr>
<tr>
<td>Spray Gr-mTiO$_2$</td>
<td>1.059</td>
<td>-20.199</td>
<td>69.957</td>
<td>14.963</td>
</tr>
<tr>
<td></td>
<td>(1.06±0.005)</td>
<td>(-19.79±0.43)</td>
<td>(67.26±2.54)</td>
<td>(14.21±0.80)</td>
</tr>
<tr>
<td>Spin mTiO$_2$</td>
<td>1.031</td>
<td>-17.039</td>
<td>65.488</td>
<td>11.503</td>
</tr>
<tr>
<td></td>
<td>(1.04±0.008)</td>
<td>(-18.12±0.96)</td>
<td>(62.62±2.50)</td>
<td>(11.76±0.29)</td>
</tr>
<tr>
<td>Spin Gr-mTiO$_2$</td>
<td>1.030</td>
<td>-19.224</td>
<td>68.199</td>
<td>13.506</td>
</tr>
<tr>
<td></td>
<td>(1.04±0.01)</td>
<td>(-18.02±0.10)</td>
<td>(65.22±4.11)</td>
<td>(12.91±0.91)</td>
</tr>
</tbody>
</table>

**Table 2.** Electrical parameters of sprayed large-area (1.1 cm$^2$) PSCs with and without graphene into mTiO$_2$ compared with the ones exploiting spin-coated mTiO$_2$. All the devices were measured under 1 sun AM 1.5G illumination.
JSC, FF and VOC values were 18.7 mA cm⁻², 0.72 and 1050 mV, respectively. By introducing graphene flakes into the mTiO₂, average JSC increased up to 22.2 mA cm⁻², while VOC and FF values did not undergo significant variations. Therefore, our champion cell exhibited 17.5% PCE, exceeding the highest PCE previously reported for a two-step process (0.1 cm² active area) CH₃NH₃PbI₃-based PSC using spin-coated mTiO₂ layer (PCE 17%) [62, 75].

The characterization of large-area (1.1 cm²) cells (see Table 2 and Figure S6) confirmed the JSC enhancement for Gr-mTiO₂-based cells with respect to that of pristine mTiO₂-based reference (from -18.5 to -20.1 mA cm⁻²).

Time-dependent PCE response (Figure S7a) and I-V curves as a function of the scan voltage direction (Figure S7b) did not evidence the presence of hysteresis [8].

The role of graphene in mTiO₂ film: electro-optical analysis

With the aim to fully understand the differences between the pristine mTiO₂ and the Gr-mTiO₂ based devices, complementary electrical measurements (Voc/Jsc vs. light intensity) were performed for each device typology.

The relation between Voc and the incident light power (Pin) (Figure 4a) allowed the recombination processes at the mTiO₂/perovskite interface to be evaluated [76, 77]. Voc vs. Pin trends recorded for all the tested device typologies showed a logarithmic increase with similar slope values (124 mV dec⁻¹ for spray reference-mTiO₂, 119 mV dec⁻¹ for spray Gr-mTiO₂ and 122 mV dec⁻¹ for spin mTiO₂ and spin Gr-mTiO₂). This means that Gr-mTiO₂ based ETL did not significantly influence charge recombination rate over a wide operating light intensity window (from 0.1 mW cm⁻² to 100 mW cm⁻²). The higher Voc absolute values recorded for Gr-mTiO₂ based device compared to that of free-graphene devices was correlated with the reduced interfacial charge recombination at TiO₂/perovskite, in accordance with previous reports [78].

Table 3. The sheet resistance of pristine mTiO₂ and the Gr-mTiO₂, measured by four-point probe system.
In addition, the variation of $J_{sc}$ vs. $P_{inc}$ was recorded, as reported in Figure 4b. Since the $I_{sc}$-$P_{inc}$ slope increases with the efficiency of charge collection at the device contacts [79], we concluded that sprayed Gr-mTiO$_2$ layer with 266 mA W$^{-1}$ slope effectively collected the photo-generated electrons from the perovskite absorber. Finally, transient $V_{oc}$ rise measurements represented in Figure 4c were carried out by suddenly switching on the 1 SUN illumination from the dark steady state condition ($t = 0$ s) and monitoring the subsequent rise in photovoltage. The time rise of $V_{oc}$ for PSC with Gr-mTiO$_2$ was shorter than the reference device. This indicated that an efficient active layer regeneration and/or charge-transfer process between the active and the transport layers occurred in presence of graphene flakes [80]. The fast rises for PSC with Gr-mTiO$_2$ can be ascribed to a fast filling and stabilization of charge trap states by injected or photogenerated electrons, reducing the availability of trap sites to mediate non-radiative recombination [81]. The rise time of $V_{oc}$ obtained for our PSCs evidenced an electron injection improvement at perovskite/mTiO$_2$ interface when mTiO$_2$ is doped with graphene [82].

According to the electrical parameter statistic graphs (Figure 3), a dual effect of the Gr-mTiO$_2$ on device performance is evidenced. First, the presence of graphene in the mTiO$_2$ scaffold can deform the perovskite grain due to ferroelectric distortion at graphene/perovskite interfaces which affects the perovskite crystallization process [78, 82]. This can cause an efficient electron injection at the Gr-mTiO$_2$/perovskite interface [58]. Second, graphene can assist the negative carrier transport within the TiO$_2$ layer by increasing electron mobility, which results in increasing the PSCs photocurrent density [83].

In order to further investigate the enhancement of the device performance through the incorporation of graphene in mTiO$_2$, the effects of the absorber layer and conductivity of TiO$_2$ layer were characterized. A four-point probe system was employed to measure the sheet resistance of pristine and Gr-mTiO$_2$. As reported in Table 3, Gr-TiO$_2$ showed a 55% increase of the conductivity with respect to that of pristine mTiO$_2$.

As a further confirmation, sprayed Gr-mTiO$_2$-based PSCs have shown an improvement in the photocurrent density which is defined by integrating IPCE over the absorption wavelength range. Actually, IPCE($\lambda$) is the product of three factors: light harvesting efficiency ($\eta_{hl}$) depending on the perovskite layer, the quantum yield of charge injection from exited perovskite to ETL and HTL ($\eta_{INJ}$) and the charge carrier collection efficiency ($\eta_{COL}$) at the electrodes (IPCE = $\eta_{INJ} \eta_{INJ} \eta_{COL}$) [84]. In addition, the $\eta_{INJ}$ is defined as the product between the electron injection ($\eta_{INJ}$) and hole injection ($\eta_{HINJ}$) efficiency, as well as collection efficiency is defined as the product between the electron collection ($\eta_{EOL}$) and hole collection efficiencies ($\eta_{COL}$) respectively.

$\eta_{INJ} = \eta_{EOL} \eta_{HINJ}$
$\eta_{COL} = \eta_{EOL} \eta_{HCOL}$

Figure 4d shows the absorption spectra of perovskite grown on both mTiO$_2$ and Gr-mTiO$_2$ scaffolds, evidencing that they are perfectly overlapped. This means that the modified Gr-TiO$_2$ layer did not affect the perovskite light harvesting properties. Consequently, since the two structures differed only in the addition of graphene within the ETL, the $\eta_{HINJ}$, $\eta_{INJ}$ and $\eta_{COL}$ can be considered equal for both structures. Therefore, enhancement of IPCE in graphene-based devices can be likely ascribable to higher $\eta_{INJ}$ at the perovskite/HTL interface and improved $\eta_{COL}$ at the PE. Such analysis agrees with the $V_{oc}$ rise and $V_{oc}/J_{sc}$ vs. $P_{inc}$ trends previously discussed.

**Figure 5.** PCE aging trends under prolonged 1 SUN white LED illumination at MPP for the tested device typologies.

One of the most crucial challenges for mesoscopic PSCs is the stability under real working condition [85]. Despite numerous efforts by the scientific community to develop more stable cells, many issues are still opened since perovskite degradation depends strongly on light, moisture, and temperature [86-88].

Based on these considerations, we compared the stability of encapsulated PSCs based on pristine sprayed mTiO$_2$ and Gr-mTiO$_2$, respectively, by exposing them continuously under 1 SUN illumination for 2 days at 50 °C and 55% relative humidity of ambient air. The I-V characteristics were progressively acquired during the ageing time at MPP. The extracted electrical parameters are reported in Figure 5, normalized to the value obtained at $t = 0$ min. Notably, the cells based on sprayed Gr-mTiO$_2$ showed a remarkable stability by retaining more than 80% of the initial PCE value.
after more than 40 h of the stress test, whereas the PCE of the spray pristine mTiO$_2$ cells decayed by 50% over the first 25 h.

As discussed in the previous section, the Gr-mTiO$_2$ has an electrical conductivity that can optimize charge collection [89-92] and separation [80,91] at the PE. The improved charge extraction at the PE drastically reduces the trapped charges accumulated at the mTiO$_2$/perovskite interface. This slows down the perovskite degradation [92]. Moreover, as discussed by Busby et al. [93] through ToF-SIMS measurements, the presence of graphene into the mTiO$_2$ limits the Ti-I bonding preserving a compact CH$_3$NH$_3$PbI$_3$ layer upon the light-induced ageing. We should also point out that 2D materials can improve thermal stability by reducing surface degradation of perovskite [94].

**Conclusion**

The field of perovskite solar cells (PSCs) is rapidly moving toward consolidating deposition processes that can be extended to large-area for industrial exploitations. In this work, we reported that the combined use of automatized spray coating techniques and graphene doping of mTiO$_2$ is an effective strategy to improve photovoltaic performances of PSCs with respect to the conventional, lab-scale device produced by spin coating process. More in detail, the PSC fabricated on a small-area with spray-coated Gr-mTiO$_2$ has shown an average power conversion efficiency (PCE) of 16.8% (max 17.5%), which is remarkably superior to that obtained for PSC using graphene-free sprayed coating (14.3%) or spray-coated mTiO$_2$ (15.1%). These results were also confirmed on large-area cells, which achieved a PCE of 14.96% using spray-coated Gr-mTiO$_2$, against 13.1% obtained by the reference PSCs. Electro-optical characterizations and transient measurements have shown that graphene doping of TiO$_2$ can improve the electron transport in ETL and charge injection at perovskite/ETL interface. In addition, Gr-mTiO$_2$ layer strongly affected the stability of PSCs under prolonged (47h) light soaking conditions by enlarging the lifetime of the devices, which retained more than 80% of the initial PCE value. These results pave the way to realize stabilized mesoscopic perovskite solar modules with a versatile, low-cost and roll-to-roll compatible printing technique.

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