Graphene-induced improvements of perovskite solar cell stability: effects on hot-carriers.

P. O'Keeffe,[†] D. Catone,^{*,‡} A. Paladini,[†] F. Toschi,[†] S. Turchini,[‡] L. Avaldi,[†] F. Martelli,[¶] A. Agresti,[§] S. Pescetelli,[§] A. E. Del Rio Castillo,^{||} F. Bonaccorso,^{||,⊥}
and A. Di Carlo[§]

[†]*CNR-ISM, Division of Ultrafast Processes in Materials (FLASHit), Area della Ricerca di Roma 1, Monterotondo Scalo, Italy*

[‡]*CNR-ISM, Division of Ultrafast Processes in Materials (FLASHit), Area della Ricerca di Roma Tor Vergata, Via del Fosso del Cavaliere, 100, Rome, Italy*

[¶]*CNR-IMM, Area della Ricerca di Roma Tor Vergata, 100 Via del Fosso del Cavaliere, Rome, Italy*

[§]*CHOSE (Centre for Hybrid and Organic Solar Energy), Department of Electronic Engineering, University of Rome Tor Vergata, Via del Politecnico 1, 00133 Rome, Italy*

^{||}*IIT - Istituto Italiano di Tecnologia, Graphene Labs, Via Morego 30, 16163 Genova, Italy*
[⊥]*BeDimensional Spa, Via Albisola 121, 16163 Genova, Italy*

E-mail: daniele.catone@ism.cnr.it

Abstract

Hot-carriers, i.e. charge carriers with an effective temperature higher than that of the lattice, may contribute to the high power conversion efficiency (PCE) shown by perovskite-based solar cells (PSCs), which are now competitive with silicon solar cells. Hot-carriers lose their excess energy in very short times, typically in a few picoseconds after excitation. For this reason, the carrier dynamics occurring on this timescale are extremely important in determining the participation of hot-carriers in the photovoltaic process. However, the stability of PSCs over time still remains an issue that calls for a solution. In this work, we demonstrate that the insertion of graphene flakes into the mesoscopic TiO_2 scaffold leads to stable values of carrier temperature. In PSCs aged over one week we indeed observe that in the graphene-free perovskite cells the carrier temperature decreases by about 500 K, from 1800 K to 1300 K, while the graphene-containing cell shows a reduction of less than 200 K after the same aging time delay. The stability of the carrier temperature reflects the stability of the perovskite nanocrystals embedded in the mesoporous graphene- TiO_2 layer. Our results, based on femtosecond transient absorption measurements, show that the insertion of graphene can be beneficial for the design of stable PSCs with the aim of exploiting the hot-carrier contribution to the PCE of the PSCs.

KEYWORDS: perovskite, graphene, solar cell, hot-carriers, ultrafast, cooling

The use of halide perovskites as the photo-active material in solar cells, photodetectors, light emitting diodes and lasers has recently undergone a rapid development.^{1,2} Much of this interest is due to the remarkable properties of these low-cost materials, such as high absorption cross sections covering almost the entire visible range (400-800 nm),³ high carrier mobility,³ long charge diffusion¹ as well as low rates of non-radiative recombination of electron-hole pairs.¹ Since the pivotal exploitation of perovskite in solar cells by Miyasaka and coworkers,⁴ who achieved a power conversion efficiency (PCE) of 3.8 %, the performances of perovskite-based solar cells (PSCs) have been rapidly improved up to a PCE of 23.3 %, ^{5,6} rivalling traditional silicon-based solar cells.⁷ The current state-of-the-art performance has been achieved by step-by-step optimization of perovskite deposition techniques that allow a fine control on the morphology of the perovskite layer,⁸ improvement of the interface engineering^{9,10} and the architecture of the devices,^{11,12} as well as acting on the perovskite composition.¹³ Nonetheless, the stability of PSCs over time still remains an issue that requires a solution. In fact, a strong research effort has been devoted to improve the lifetime of the perovskite layer,¹⁴⁻¹⁷ which is susceptible to degradation by oxidation,¹⁴ photo-degradation¹⁴ and reaction with water vapour.^{12,18,19} In this context, the structural properties of the electron transport layer (ETL) plays a primary role in the overall efficiency of PSCs. The addition of graphene and related 2D materials (GRMs)²⁰⁻²² to the ETL, has a beneficial effect on the stability of PSCs²³ and large-area modules.²⁴ Moreover, the presence of GRMs also enhances the PSC performance, thanks to the improvement of the crystalline quality at the interface between the mesoporous layer of TiO₂ (m-TiO₂) and the perovskite nanocrystals embedded in m-TiO₂.²⁵

Despite the rapid development of perovskite-based devices, the ultrafast dynamics of hot-carriers (i.e. with an effective temperature higher than that of the lattice) is still far from being completely understood, even though it is known that their efficient collection may increase the PCE of the solar cells, overcoming the Shockley-Queisser limit.^{26,27} The hot-carriers typically lose most of their excess energy in less than 10 ps after excitation.²⁸ For this

reason, the carrier dynamics occurring on this ultrashort timescale are extremely important in determining the participation of hot-carriers in the photovoltaic process.^{3,29,30}

On the timescale ranging from tens of femtoseconds to hundreds of picoseconds, it is important to conceptually distinguish two processes: carrier thermalization and hot-carrier cooling.

The carrier thermalization process is dominated by carrier-carrier scattering in which the photoexcited carriers exchange energy, forming a thermal distribution defined by a specific temperature (T_C). This process occurs on a timescale of tens/hundreds of femtoseconds.³⁰

The hot-carrier cooling involves exchange of energy between carriers and phonons, bringing the carriers into thermal equilibrium with the lattice. This process occurs on a timescale ranging from picoseconds to tens/hundreds of picoseconds.³¹ The study of charge generation, carrier thermalization, hot-carrier cooling and charge transfer processes in perovskites, provides key information on the carrier dynamics in perovskite-based devices, boosting the development of new materials with tailored optical and photovoltaic properties. For these reasons, the control of both carrier thermalization and cooling process could improve the optimization of the extraction and collection of the hot-carriers.

In this work, we investigate the role of graphene flakes on the PCE and stability of PSCs, using femtosecond Transient Absorption (TA) spectroscopy of two PSC configurations, i.e.

Glass+FTO/c-TiO₂/m-TiO₂/CH₃NH₃PbI₃/Spiro-OMeTAD/Gold (PSC-NoG) and

Glass+FTO/c-TiO₂/m-TiO₂+Graphene/CH₃NH₃PbI₃/Spiro-OMeTAD/Gold (PSC-G).

The studied PSCs present two perovskite layers: a capping layer of large-sized perovskite crystals with dimensions of ~ 500 nm, and an ETL composed of small-sized perovskite crystals with dimensions of 20-40 nm, spatially restrained within the m-TiO₂ layer, deposited on a compact TiO₂ (c-TiO₂), acting as a hole-blocking layer.^{25,32,33} Graphene flakes (see Supporting Information (SI) for the characterization details), produced by liquid phase exfoliation of pristine graphite,^{34,35} were added only into the ETL of PSC-G. A schematic representation of the studied PSCs is presented in Figure 1.

Our TA measurements provide important information on carrier dynamics within the per-

ovskite crystals by spectroscopically distinguishing between the small crystals of the ETL and the large crystals of the capping layer.³⁶ Furthermore, we show that the addition of graphene into the m-TiO₂ reduces the degradation of the small crystals in the mesoporous layer with ageing, preserving the stability and hence the high PCE of PSC-G over time. [REMOVED] In fact, the addition of graphene flakes has already been demonstrated to reduce the moisture penetration, which plays a major role in perovskite ageing. [REMOVED] In particular, we use TA spectroscopy to monitor the carrier temperature in perovskite layers, in order to study how the carrier dynamics in PSCs are affected by the addition of graphene into the ETL.

Figure 1: Schematic representation of the layer structure of the studied PSCs. HTL: spiro-OMeTAD. ETL in PSC-G: m-TiO₂ + graphene + perovskite. ETL in PSC-NoG: m-TiO₂ + perovskite. c-TiO₂: compact TiO₂ hole-blocking layer. FTO: Fluorine doped Tin Oxide. The capping layer is composed by large-sized perovskite crystals with dimensions of about 500 nm. The ETL is composed by small-sized perovskite crystals with dimensions of 20-40 nm, spatially restrained within the m-TiO₂ layer.

Transient absorption spectroscopy probes a number of dynamical processes: a) attenuation of the absorption due to band filling (photo-bleaching - PB),³ b) absorption of newly populated excited states (photo-induced absorption - PIA),³⁷ c) photo-induced light emis-

sion,³⁷ d) shifts in the linear spectrum, which can manifest themselves as either PIA or PB and can be caused by effects such as band gap renormalization,³ and e) photomodulation of the refractive index.²⁸ Therefore TA spectroscopy is extensively used to study both mesoscopic^{32,36,38} and planar^{3,28,30,39} structured halide perovskites, investigating the processes which contribute to the complex dynamics of a PSC device, i.e. the hot-carrier cooling,²⁸ carrier trapping,⁴⁰ bimolecular and Auger recombination,⁴¹ long-range transport of electrons and holes,^{32,42} carrier mobility⁴³ and hot-hole injection into the Hole Transport Layer (HTL).⁴⁴ For this reason, many aspects have to be taken into account when discussing the dynamics of PSCs, e.g. the morphology of the perovskite layer,^{32,42,45} the formation of excitons followed by dissociation or direct formation of free carriers,⁴¹ the stability of the PSC (whose degradation may lead to formation of PbI_2 ⁴⁶), the pump fluence³⁹ and whether the perovskite consists of a single crystal, a polycrystalline thin-film⁴² or forming part of a working cell.^{3,28}

The TA spectra were all acquired in transmission with a pump of 3.1 eV and a probe in the 1.5 - 2.8 eV energy range. The measurements were performed using a pump laser fluence of $9.1 \mu\text{J}/\text{cm}^2$ that corresponds to an estimated initial carrier density of $7.0 \times 10^{17} \text{cm}^{-3}$ that is below the onset of the hot-phonon bottleneck.³⁹ The false-colour map of the TA spectra for the as-prepared PSC-G pumped at 3.1 eV is shown in Figure 2. The TA map presents two PIA regions (positive signals labelled PIA_1 and PIA_2) and two PB regions (negative signals labelled PB_1 and PB_2).

Figure 2: False-colour map of transient absorption spectra obtained for an as-prepared PSC-G pumped at 3.1 eV with an initial carrier density of $7.0 \times 10^{17} \text{cm}^{-3}$. The probe energy on the y-axis and the pump-probe time delay on the x-axis are reported. The map presents two photo-induced absorption regions (positive signals labelled PIA₁ and PIA₂) and two photo-bleaching regions (negative signals labelled PB₁ and PB₂).

In early models,^{47,48} the PB features (PB₁ at 1.65 eV and PB₂ at 2.58 eV) were assigned to band state filling of two valence bands and a single conduction band. A new model suggests that the observed absorption bleaching involves two valence bands and two conduction bands.³³ Moreover, Yang *et al.*³⁹ have modelled the entire energy region encompassing PIA₁, PB₁ and PIA₂ using a single model, involving continuum and exciton effects as well as band gap renormalization. In any case, excitonic effects play a negligible, if any, role in the hot-carriers dynamics.^{28,39,41} In general, it is impossible to completely separate all these contributions and consider them independently to explain the spectroscopic response of a PSC.

Figure 3 reports the TA spectra in the PB₁ energy region 1.55-2.0 eV, acquired at a pump-

119 probe time delay of 0.75 ps for as-prepared (Figure 3 (a)) and aged (Figure 3 (b)) PSC-G
 120 (dark blue line) and PSC-NoG (light blue line). We have investigated only the PB_1 region
 121 because the other regions (PB_2 , PIA_1 , PIA_2) do not give any relevant information about the
 122 degradation of the devices induced by the ageing. The full energy range of the TA spectra
 123 acquired in these conditions is reported in Figure S2 of the SI. The PB_1 feature shows two
 124 distinct peaks at 1.64 eV (PB_{1A}) and 1.66 eV (PB_{1B}) that we assign to absorption bleaching
 125 in the large crystals of the capping layer and in the small crystals of the mesoporous layer,
 126 respectively. This assignment is supported by the recent literature that reports a signifi-
 127 cant blue-shift for the absorption onset,⁴⁹ photoluminescence signal^{38,45} and PB peak^{28,36}
 128 for the mesostructured small crystals with respect to the large crystals in the capping layer.
 129 The PSC-NoG and PSC-G cells investigated in this work, were both synthesized with a
 130 PbI_2 concentration of 285 mg/ml instead of 500 mg/ml, usually employed for highly effi-
 131 cient solar cells,⁵⁰ obtaining thicknesses of about 70 nm and 150 nm for the capping and
 132 mesoporous layers, respectively (see details in Methods). This PbI_2 concentration produces
 133 a thinner capping layer than that obtained by using 500 mg/ml (170 nm).⁵⁰ For this reason
 134 the thicknesses of the capping and mesoporous layers are thin enough to avoid the complete
 135 absorption of the pump and probe radiation, thus allowing the PB signals coming from both
 136 small and large crystals to be acquired in the same TA spectrum, as reported in Figure 3
 137 (a). To confirm the assignment of PB_{1A} and PB_{1B} we have also performed measurements
 138 on a PSC synthesized without graphene, with a higher PbI_2 concentration (500 mg/ml) and
 139 excited from the side of the thick capping layer. The TA spectrum obtained (see Figure S7
 140 in SI) does not exhibit the PB_{1B} peak related to the small crystals and only shows the peak
 141 at 1.64 eV assigned to the large crystals in the capping layer (PB_{1A}).

Figure 3: Transient absorption spectra acquired at pump-probe time delay of 0.75 ps for (a) as-prepared and (b) aged PSC-NoG (light blue line) and PSC-G (dark blue line). Both the cells are pumped at 3.1 eV with an initial carrier density of $7.0 \times 10^{17} \text{cm}^{-3}$. The photo-bleaching signal shows two distinct peaks at 1.64 eV (PB_{1A}) and 1.66 eV (PB_{1B}) assigned to the absorption bleaching in the large crystals of the capping layer and in the small crystals of the mesoporous layer, respectively.

The relative intensity of the PB_{1A} and PB_{1B} features and the profiles of the TA spectra are similar for the as-prepared PSC-NoG and PSC-G, as shown in Figure 3 (a), suggesting that the addition of graphene flakes during the synthesis does not significantly affect the formation of small and large crystals. In fact, the growth of the small crystals occurs within the m- TiO_2 layer, and their sizes are simply due to the spatial confinement imposed by the TiO_2 mesopores.²⁵ On the contrary, Figure 3 (b) shows differences in the TA spectra of PSC-NoG and PSC-G acquired after one week of ageing. In particular, while the relative intensities of PB_{1A} and PB_{1B} are unchanged in the spectra of PSC-G, they are different in

those of PSC-NoG when compared to the as-prepared condition. Moreover, the values of the ratio between PB_{1B} and PB_{1A} (calculated using the averaged values of 13 points centred around the maximum of the bleaching signals) of the aged PSC-NoG always remain lower than those of the aged PSC-G over the entire time range explored, as shown in Figure S8. This behaviour suggests that in PSC-NoG, the higher degradation of small crystals with respect to large crystals over time induces the intensity reduction of the PB_{1B} with respect to PB_{1A} . This is in agreement with a recent work in which perovskite back-conversion into PbI_x and PbO_x species was demonstrated together with the iodine diffusion and its role in the degradation of the m-TiO₂ layer (i.e., the Ti-I bonding).⁵¹ For this reason, the unchanged ratio observed here in PSC-G indicates that graphene plays a protective role by partially blocking the iodine diffusion from perovskite into the m-TiO₂ layer, and eventually increasing the stability of the small crystals over time.⁵¹ Moreover this fact can be related to the property of graphene to reduce the moisture penetration,⁵² which plays a major role in perovskite ageing and degradation,⁵³ and is also consistent with the observed increase of the thermal stability of perovskite by grain boundary passivation using fullerene additives⁵⁴ and boron nitride.⁵⁵ Moreover, Figure 3 (b) also exhibits another difference between the TA spectra of PSC-NoG and PSC-G: the photo-bleaching signal of PSC-NoG is less broadened (grey region) with respect to that of the PSC-G, which remains unchanged after one week of ageing. This difference can be understood after discussing how the shape of the high-energy tail is related to the temperature of the hot-carriers.

The high-energy tail of PB_1 is directly related to T_C at a given pump-probe time delay.^{39,56} A generally accepted method to extract the T_C from the photo-bleaching signal consists of fitting the high-energy tail with a simple Maxwell-Boltzman function (see SI for details). In general, a broader high-energy tail corresponds to a higher T_C .³⁹ Moreover, small crystals exhibit a longer hot-carrier cooling lifetime with respect to large crystals, suggesting a weaker interaction between carriers and phonons in the former.³⁶ In as-prepared PSCs the

177 slope of the high-energy tail is mainly given by the contribution of small crystals, however,
 178 in aged PSC-NoG the contribution of small crystals decreases due to their degradation. For
 179 this reason the slope of the high-energy tail in aged PSC-NoG is more influenced by the
 180 contribution of the large crystals. In other words, after 0.75 ps from the initial excitation
 181 the PSC-G has preserved the carriers at a higher temperature with respect to the PSC-NoG.
 182 This difference is also observed after 3 ps, as reported in Figure S9 of SI. The shift toward
 183 lower energies of the PB_{1B} peak for aged PSC-NoG compared to the PSC-G, is due to the
 184 decreased contribution of the signal relative to the small crystals that undergo a stronger
 185 degradation than the large crystals. Moreover, considering that the T_C for aged PSC-NoG is
 186 more influenced by large crystals with respect to the PSC-G where the stability over time of
 187 small crystals is preserved by graphene flakes, the observed temperature reduction confirms
 188 a faster cooling of the hot-carriers in large crystals.³⁶

Figure 4: Carrier temperature (T_C) as a function of pump-probe time delay (from 0.4 to 3 ps) for (a) as-prepared and (b) aged PSC-NoG (light blue line) and PSC-G (dark blue line). Both cells are pumped at 3.1 eV with an initial carrier density of $7.0 \times 10^{17} \text{ cm}^{-3}$.

Figure 4 reports the T_C as a function of pump-probe time delay (from 0.4 to 3 ps) for as-prepared and aged PSC-NoG (light blue line) and PSC-G (dark blue line). The T_C dynamics are reported from a time delay of 0.4 ps onwards as prior to this delay the carrier thermalization and cooling processes are still in a non-equilibrium state and therefore no T_C can be determined for the carrier distribution. In the case of as-prepared PSCs (see Figure 4 (a)), T_C has a similar initial value (1650-1800 K) and trend for both graphene-containing and graphene-free cells, demonstrating that the presence of graphene does not affect the temperature dynamics of hot-carriers. The two-component exponential decay observed in both cases with time constants of about 400 fs and 15-20 ps (see Table S1), is consistent with the timescales observed in literature.^{31,57} In those works, the sub-picosecond timescale has been assigned to hot-hole cooling process,⁴⁸ while the slower process is assigned to the scattering of electrons from the M to the Γ points of the band structure of the perovskite.³¹ Furthermore, the small crystals show a slower carrier thermalization rate with respect to large crystals.³⁶ With this consideration in mind, the comparison of T_C dynamics for the two types of PSCs after one week of ageing acquires an important meaning (see Figure 4 (b)). In particular the T_C dynamics and initial value for PSC-G are similar to those under the as-prepared conditions. This behaviour indicates once more that the stability of the small crystals is favoured by graphene. On the other hand, at a time delay of 0.4 ps the T_C of the PSC-NoG is significantly lower (about 1300 K) than the T_C both in the as-prepared condition and in the cell with graphene (about 1800 K in both cases). Even though the initial hot-carrier temperatures of the two aged PSCs are clearly different (T_C difference of about 500 K), the decay time constants remain similar to those observed in as-prepared conditions (see Table S1). This behaviour indicates that the hot-carrier cooling, which takes place on the time scale of picoseconds, is not sizeably affected by the ageing of the PSCs. For this reason, we believe that the T_C difference arises from an overall faster thermalization of the carriers after excitation, occurring at time delays shorter than 0.4 ps. In other words, the graphene in the PSC protects the integrity of the small crystals in the mesoporous layer

216 during the ageing time, preserving the temperature of the carriers for a longer time after
 217 excitation. Moreover, the theoretical model of Volonakis and Giustino⁵⁸ suggests that the
 218 graphene-perovskite interface allows a more efficient hot-carrier extraction, hindering the
 219 electron-hole recombination. It has been also recently speculated that the thermalization
 220 is the critical mechanism determining the efficiency of hot-carrier extraction.³⁰ With these
 221 considerations in mind, our findings provide the spectroscopic tools for the design of new
 222 perovskite-based cells aimed at exploiting hot-carrier extraction and collection. Indeed PSC-
 223 NoG presents a greater reduction of power conversion efficiency with respect to PSC-G,
 224 retaining 93% (reduction of 7%) of the initial PCE after one week of ageing while PSC-NoG
 225 only 86% (reduction of 14%). The details about the PCE of both samples are reported in
 226 Figure S12.

227 In conclusion, ultrafast optical measurements on encapsulated graphene-free and graphene-
 228 containing perovskite solar cells show two peaks in the lowest photobleaching band (PB_1),
 229 which we have assigned to light absorption in the small perovskite crystals (20-40 nm) of the
 230 mesoporous layer (PB_{1B} - 1.66 eV) and in the larger crystals (500 nm) of the capping layer
 231 (PB_{1A} - 1.64 eV). We have demonstrated that the addition of graphene to the mesoporous
 232 TiO_2 layer during the fabrication process of the PSCs plays a key role in the stability over
 233 time of the small perovskite crystals. This information has been inferred from the change
 234 of the relative intensities of the associated photo-bleaching signals observed in the transient
 235 absorption spectra for the as-prepared and aged PSCs with and without graphene. The
 236 ultrafast dynamics of the PSCs have revealed that while both as-prepared graphene-free and
 237 graphene-containing PSCs exhibit similar values of hot-carrier temperatures as a function
 238 of the pump-probe time delay, the aged graphene-free PSC presents lower carrier tempera-
 239 tures with respect to the aged graphene-containing PSC. This difference arises from a faster
 240 thermalization of the carriers occurring in the aged graphene-free PSC as a result of the
 241 degradation of its small perovskite crystals. The stability of the small perovskite crystals
 242 over time is also confirmed by the retained carrier dynamics and carrier temperatures in the

aged PSC. These features further demonstrate the beneficial effect of graphene also on the short timescales and more generally that the combination of 2D-3D materials systems may lead to novel properties and devices.^{59,60} Although our results do not link the hot-carrier dynamics to the cell efficiency, we think that the insertion of graphene will be of great utility for the design of stable PSCs capable of exploiting hot-carrier extraction and collection that could, in turn, lead to an enhancement of the power conversion efficiency.

Methods

Materials preparation. Graphene was obtained by liquid phase exfoliation of graphite. Briefly, 10 g of graphite (150 mesh, Sigma Aldrich) was dispersed in 1000 ml N-methyl-2-pyrrolidone (NMP, Sigma Aldrich) and dispersed using an ultrasonic bath for 6 hours, immediately after ultracentrifuged at 17000 g for 50 min at 15 °C using a Optima XE-90, Beckman Coulter, ultracentrifuge equipped with a SW32Ti rotor. Then, 80% of the supernatant was collected by pipetting. Optical absorption spectroscopy was used to determine the concentration of the graphene flakes in dispersion. The collected supernatant was successively dried using a rotary evaporator (at 70 °C, 5 mbar). Afterwards, the dried flakes were dispersed in 50 mL of ethanol by means of ultrasonication for 10 min, followed by a centrifugation process carried out at 800 g for 30 minutes at 15 °C. The sediments were subsequently collected and the supernatant discarded. This process of decantation was repeated twice, in order to wash out the NMP residuals. Finally, an ethanol/water [80:20] mixture was prepared to disperse the graphene flakes with a concentration of 0.9 g/l. The characterization of the graphene dispersion can be found in the SI.

Device Preparation. F-doped tin oxide (FTO) coated glasses (Dyesol 7 $\Omega \times \text{cm}^{-1}$; 25x25 mm) were patterned by laser ablation and subsequently washed with liquid detergent and deionized water. The substrates were cleaned by ultrasonic bath with acetone and 2-propanol for two sequential cycles lasting 15 minutes each. A solution composed of acetylacetone (2 ml), titanium diisopropoxide (3 ml) and ethanol (45 ml) was deposited onto the conductive glass substrate by spray pyrolysis at 455 °C, yielding the compact TiO_2 hole-blocking layer (c- TiO_2). A m- TiO_2 nanocomposite film (particle size 20 nm) overlaps the c- TiO_2 / FTO substrates and it was deposited by spin coating the TiO_2 paste (Dyesol 18 NRT paste diluted in ethanol/water 1:5) at 2000 rpm for 20 seconds. The graphene doped m- TiO_2 was made by adding 1% v/v of graphene dispersion to the TiO_2 diluted paste. The mesoporous film was sintered at 480 °C for 30 minutes in air for both TiO_2 pastes. The single cation perovskite layer was coated onto the prepared substrates by a sequential de-

position of PbI_2 (285 mg/ml, in dimethylformamide) and $\text{CH}_3\text{NH}_3\text{I}$ (MAI) (10 mg/ml in 2-propanol). During the two step deposition firstly, the PbI_2 solution was deposited by spin coating for 10 seconds at 6000 rpm, then the as coated wet film was dipped in a MAI solution for 15 min. Lastly, the $\text{CH}_3\text{NH}_3\text{I}_3$ active layer formation was completed during the second step by annealing the substrate at 80 °C and by rinsing with anhydrous 2-propanol. The devices were completed by adding a HTL topped with a thermally evaporated gold back contact (100 nm). The HTL consists of 73.2 mg/ml solution of 2,20,7,70-tetrakis-(N,N-dimethoxyphenylamine)9,9'-spirobifluorene (Spiro-OMeTAD) deposited by spin coating 2000 rpm for 20 sec on top of the perovskite layer. The Spiro-OMeTAD solution was doped by 7.2 μl of cobalt FK209 (stock solution 375 mg in 1 ml acetonitrile), 11.4 μl of tert-butylpyridine (TBP) and 12 μl of Lithium Bis(Trifluoromethanesulfonyl)Imide (Li-TFSI) solution (520 mg in 1 ml of acetonitrile).

Electrical Characterizations and Shelf-life Tests. The active areas of devices (0.1 cm^2) were tested in air atmosphere with encapsulation under a solar simulator (ABET Sun 2000, class A) at AM1.5 and 100 mW cm^{-2} illumination conditions, calibrated with a certified reference Si Cell (RERA Solutions RR-1002). Incident power was measured with a Skye SKS 1110 sensor. The Sun Simulator class was measured with a BLACK-Comet UV-Vis spectrometer. Shelf-life tests were performed in dark and open circuit condition, dry atmosphere with HR<30% and at room temperature. Maximum Power Point (MPP) measurements were carried out under a solar simulator (ABET Sun 2000, class A) at AM1.5 and 100 mW cm^{-2} illumination conditions. Incident Photo-Current conversion Efficiency (IPCE) spectra acquisition were performed by means of a homemade setup. The as-prepared PSC-G and PSC-NoG were stored under anhydrous and dark conditions for one week and then used for aged TA spectroscopy measurements. Further technical details are provided elsewhere.²¹

Femtosecond Transient Absorption Spectroscopy. The pump-probe experiments were performed using a laser system consisting of a 800 nm, 1 kHz, 4 mJ, 35 fs chirped pulse amplifier seeded by a Ti:Sa oscillator. The pump pulse (400 nm) was produced by

second harmonic generation while the probe was generated by focusing 3 μJ of 800 nm light into a rotating CaF_2 crystal. The optical layout of the commercial transient absorption spectrometer (FemtoFrame II, IB Photonics) consisted of a split beam configuration in which 50 % of the white light (350 - 800 nm) passes through the sample while the remainder was used as a reference to account for pulse to pulse fluctuations in the white light generation. The pump pulse is loosely focused (circular spot with a diameter of about 700 μm) onto the sample with variable power density of 4.6-25.5 $\mu\text{J}/\text{cm}^2$. The spot diameter of the probe pulse is approximately 150 μm and was scanned in time by varying the length of its optical path. All experiments were performed with linear polarization for both pump and probe pulses. The instrument response function was measured to be approximately 50 fs. More experimental details on the setup can be found elsewhere.^{61,62}

Acknowledgements

DC, PO'K and ST acknowledge funding from PRIN project no. 2015CL3APH. FB, AA, SP and AEDC acknowledge European Union's Horizon 2020 research and innovation programme under grant agreement No. 785219 – GrapheneCore2.

Author Contributions

DC, PO'K, AP and FT conceived the experiment, performed the transient absorption measurements and analysed the data. AEDC and FB prepared and characterized the graphene material. AA, SP and AEDC prepared the samples and performed the cell characterization and shelf-life tests. All authors discussed the data and contributed to the manuscript.

Additional Information

Supplementary Information is available in the online version of the paper.

Graphene characterization. TA spectra acquired at different time delays. Electrical characterization of complete devices (forward and reverse scan J-V curves, the performance statistics and the incident photon to current conversion efficiency spectra). Ratio between active small and large crystals TA signals as a function of time delay. Details of fitting procedure. Normalized power conversion efficiency. Absorption spectra of as-prepared and aged samples.

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