Beneficial Role of Reduced Graphene Oxide for Electron Extraction in Highly Efficient Perovskite Solar Cells

Kyung Taek Cho, a Giulia Grancini, a Yonghui Lee, a Dimitrios Konios, b Sanghyun Paek, a Emmanuel Kymakis, b and Mohammad Khaja Nazeeruddin a

a. Group for Molecular Engineering of Functional Materials, Institute of chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne, Sion CH-1951, Switzerland
b. Center of Materials Technology and Photonics & Electrical Engineering Department School of Applied Technology Technological Educational Institute (T.E.I) of Crete Heraklion, 71 004 Crete, Greece

In this work we systematically investigated the role of reduced graphene oxide (rGO) in hybrid perovskite solar cells. By mixing rGO within the mesoporous TiO2 (m-TiO2) matrix high efficient solar cells with power conversion efficiency (PCE) of 19.54% was realized. In addition, the boosted beneficial role of rGO with lithium doped m-TiO2 as electron funnel to the TiO2 was demonstrated by a combination of structural and optical analysis.

Ever since its isolation in 2004,1 graphene had a huge impact on applications in optoelectronic and photon energy conversion, owing to its unique electronic, optical and mechanical properties.2-5 The development of solution-processable graphene, such as the chemical exfoliation of graphite into graphene oxide (GO), allowed the functionalization and processing of graphene, extending its use in the different layers of solution processable solar cells.6,7 Among different solar cell technologies, hybrid perovskite -based solar cells (PSCs) have been dominating the interest of the scientific research community for their impressive technological development with power conversion efficiency beyond 22% in a short of six years of research.8 However, further improvements are necessary to optimize the PSC device operation and stability, and enhance the device performance. From this point, mixed graphene-based derivatives have been proposed to further enhance the device properties.7 Used in various form and with different functionalities, either incorporated in mesoscopic or in planar device configuration,9,10 functionalized rGO derivatives have been successfully employed as charge extraction in electron transport layer9,11,12 or hole transport layer12 in PSCs. It has been demonstrated its ability to effectively reduce the charge recombination pathways and decrease the leakage currents, with a similar role as when employed in organic solar cells.14-16 However, all of device efficiencies reported are limited to less than 14% and the perovskite was not formed as a perfect film, which casts the doubt on the real beneficial role of rGO on high-efficiency PSCs. In contrast to many application of carbon-based materials that are usually introduced at the perovskite/TiO2 or perovskite/hole transport materials (HTM) interfaces or in substitution of the HTM itself,17,18 here we propose a systematic study by exploring three different configurations as shown in Fig. 1.
We integrated the rGO: 1) in the HTM, doped 2,2',7,7'-tetrakis(N,N'-di-p-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD), 2) in the matrix of the active mixed perovskite and 3) within the electron transport layer, the mesoporous TiO$_2$ (m-TiO$_2$). In this study mesoscopic PSCs are composed of a fluorine doped tin oxide (FTO), a dense and mesoporous TiO$_2$ layer, the mixed perovskite layer in the form of (FAPbI$_3$)$_{0.85}$(MAPbBr$_3$)$_{0.15}$, the spiro-OMeTAD, and lastly a gold counter electrode.

We investigate the effect of the introduction of the rGO flakes in each different layer comparing the results with standard cells without rGO. Furthermore, to better examine the exact effect of rGO in the electron transport layer, we compared devices with and without treating the TiO$_2$ surface with lithium (Li), which has been recently proven to improve the device performances, by facilitating the interfacial electron injection.

A schematic of different device architectures is illustrated in Fig. 1a-c, where rGO has been included in the m-TiO$_2$ layer, mixed perovskite layer, and spiro-OMeTAD layer, respectively. Energy level diagrams are inserted in the cartoon in Fig. 1d-f.

![Figure 1](image1.png)

**Figure 1.** Illustration of the solar cells architectures fabricated with rGO in each layer: a) TiO$_2$ mesoporous layer, b) mixed perovskite layer and c) spiro-OMeTAD layer. The corresponding energy levels diagram of these three devices (d-f). These energy levels are based on the individual materials. Within the solar cell and under illumination there will be a relative shift.

![Figure 2](image2.png)

**Figure 2.** J-V curves of the best performing devices for each architecture described in Fig. 1, where measured under AM 1.5 solar irradiation of 100 mW/cm$^2$. In the inset the table is summarising the solar cell parameters.

In this study mesoscopic PSCs are composed of a fluorine doped tin oxide (FTO), a dense and mesoporous TiO$_2$ layer, the mixed perovskite layer in the form of (FAPbI$_3$)$_{0.85}$(MAPbBr$_3$)$_{0.15}$, the spiro-OMeTAD, and lastly a gold counter electrode. We investigate the effect of the introduction of the rGO flakes in each different layer comparing the results with standard cells without rGO. Furthermore, to better examine the exact effect of rGO in the electron transport layer, we compared devices with and without treating the TiO$_2$ surface with lithium (Li), which has been recently proven to improve the device performances, by facilitating the interfacial electron injection. A schematic of different device architectures is illustrated in Fig. 1a-c, where rGO has been included in the m-TiO$_2$ layer, mixed perovskite layer, and spiro-OMeTAD layer, respectively. Energy level diagrams are inserted in the cartoon in Fig. 1d-f.
The characterization of rGO, along with the calculations of the rGO HOMO level, being approximately $-4.96$ eV and LUMO level of $-3.95$ eV, are explained in Fig. S1 and S2. As the energy level of rGO is lower than the TiO$_2$ and mixed perovskite, we expect that the photoexcited electron can funnel through the rGO plates. The cross-sectional scanning electron microscopy (SEM) images of the four studied perovskite solar cells architectures are provided in Fig. S3, showing the layered device structure, as depicted in Fig. 1. The solar cells J-V curves of the best devices for each architecture along with the device parameters are shown in Fig. 2. Depending on in which layer the rGO has been added, the performances vary dramatically. It is found that the presence of rGO has a strong positive impact in improving the device performances when mixed within the m-TiO$_2$. Considering the controller (without the rGO) provides a PCE of 18.8% (see table in the inset of Fig. 2), the mixed rGO and m-TiO$_2$ shows an improvement leading to a PCE=19.5%.

When the rGO is mixed within spiro-OMeTAD or with the perovskite (Fig. 1b and c), we observe no significant improvement in the device performances, showing similar PCE or even worse (table in the inset of Fig.2). Interestingly, these results are quite in contrast to what observed in literature indicating that rGO plays always a positive role for improving PCE of PSCs.\textsuperscript{9-11, 23, 24} The reduced photovoltaic performance when rGO is mixed either with the perovskite or with the spiro-OMeTAD can be attributed to a detrimental effect of the rGO in the device structure. This observation comes from the analysis of SEM top-view (Fig. 3). In Fig. 3a and 3c the top-surface of the perovskite film and of the complete cell with spiro-OMeTAD are compared to the ones that include the rGO (Fig. 3b and 3d, respectively). When rGO is incorporated either within the perovskite film or even with the spiro-OMeTAD the film is not homogeneous anymore, so the rGO is responsible for the formation of nano-flakes that disrupt the crystal quality. This causes the additional shunt pathways which negatively affect the perovskite device performances. Direct pathways between the perovskite and the top gold electrode or the bottom TiO$_2$ and spiro-OMeTAD can be easily generated by the rGO flakes, increasing the possibility of charge

\textbf{Figure 3.} SEM top view of the sample without and with the rGO mixed a,b) with perovskite materials, and c,d) with the spiro-OMeTAD. Note the presence of aggregates on the surface in the second case (b, d), which came from rGO and can create shunt pathways connection between m-TiO$_2$ and spiro-OMeTAD or perovskite and gold.
recombination and leading overall to the reduced device performances observed. Note that this effect is even worse when the rGO is mixed within the perovskite that creates unwanted electron leakage flow toward spiro-OMeTAD (Fig. S4). On the contrary, when we added the rGO in the m-TiO₂ layer, the PCE of solar cells shows the highest performances. Both the VOC and FF are improved, resulting in the best performing device with PCE maximum of 19.54%. We conclude that only when the rGO is mixed with the m-TiO₂ it has a beneficial effect on the PSC performance.

To further unveil the effects of the rGO incorporation in the m-TiO₂ layer, we also fabricate additional devices without the Li treatment on TiO₂ electrode. Li doping is usually performed for the high efficient solar cells, since it has a beneficial role in passivating the surface traps and in improving the electron injection. We compare in Fig. 4a the J-V curves with and without the Li-doping on the pure TiO₂ electrodes and including the rGO. Note, indeed, that without the Li doping the performances are overall reduced to PCE around 17%, as shown in Table 1. This comparison might be fairer than comparing only m-TiO₂ based perovskite solar cell to the one containing both Li and GO as shown in Ref. 16.

**Table 1.** Comparison of the Device results without and with rGO (with no Li treatment).

<table>
<thead>
<tr>
<th></th>
<th>Voc (V)</th>
<th>Jsc (mA/cm²)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without rGO</td>
<td>1.081</td>
<td>22.548</td>
<td>0.718</td>
<td>17.51</td>
</tr>
<tr>
<td>With rGO</td>
<td>1.063</td>
<td>22.74</td>
<td>0.737</td>
<td>17.8</td>
</tr>
</tbody>
</table>

We note that the difference from insertion of rGO on undoped TiO₂ electrode is quite lower compared to the Li-doped devices. Even though the device using rGO without the Li passivation shows the increased FF and current density, suggesting a better electron injection pathway, the VOC is little reduced. From our results it is clear that only the combination of rGO on Li-doped m-TiO₂ provide the best performances.

![Figure 4](image)

**Figure 4** a) J-V characteristics of the solar cells whose parameters are presented in Table 1. b) Normalized Photoluminescence decay upon excitation at 460 nm from the m-TiO₂ side for the different samples investigated as in the legend. Solid line represent the outcome of the exponential fitting. See Table S1 for fitting parameters. All the samples have been encapsulated to prevent any oxygen or moisture degradation.

To elucidate in-depth the role of the rGO we monitor the photoluminescence (PL) decays of the devices including the rGO in the m-TiO₂. The presence of rGO induces a quenching of the PL signal (see Fig. S5). Fig. 4b shows the PL dynamics at 770 nm upon excitation at 460 nm. The controller sample not treated either with Li or rGO
shows a long living decay out of our temporal window reflecting the intrinsic electron
hole recombination dynamic in the perovskite. On the contrary, we observe that the
presence of the rGO quenches the PL signal. This might indicate that, among other
processes, electron transfer is facilitated in presence of the rGO, acting as a funnel.
The quenching happens on a time scale of few tens of ns. Table S1 shows the
parameters derived from exponential fitting of the PL decays. On the other side, when
both rGO and Li dopants are mixed with the m-TiO₂ an even faster quenching
component is observed, resulting in an initial PL decay within 1 ns, which correspond
to the resolution of our system. This can be attributed to a more efficient and faster
electron injection at the treated interface due to the synergic positive effects of both in
improving the electron extraction. For sake of completeness, note that no differences
are observed when we probe the PL decay upon exciting selectively the perovskite
capping layer (Fig. S6), supporting the role of the rGO exclusively on the interfacial
dynamics.

Conclusions

The overall study presented a throughout analysis of the role of rGO integrated in
perovskite based solar cell, elucidating its main role in improving the electron
transport when mixed with the m-TiO₂. In the other case, unwanted shunt resistance
pathways are generated if the rGO is incorporated with the perovskite itself or with the
spiro-OMeTAD, reducing the overall device performances. In addition, from the
synergy effect of the rGO and Li doping on TiO₂ the device yielded a superior
efficiency of 19.54%, which is ascribed to the beneficial role of rGO in funnelling
electrons through the electron transporting layer. We believe that our combined system
of rGO and Li treatment may pave the way for further developing and optimizing the
electron transport and collection behind high efficient PSCs.

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References

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   428.


Supporting Information

Experimental Section

Preparation of Graphene Oxide (GO)\(^1\)

GO was prepared from graphite powder (Alfa Aesar, ~200 mesh) according to a modified Hummers’ method. In more detail, graphite powder (0.5 g) was placed into a mixture of sulfuric acid, H\(_2\)SO\(_4\) (40 mL, 98%) and sodium nitrate, NaNO\(_3\) (0.375 g). The mixture was then stirred and cooled in an ice bath. While maintaining vigorous stirring, potassium permanganate, KMnO\(_4\) (3.0 g) was then added in portions over a period of 2 h. The reaction mixture was left for 4 h in order to reach room temperature before being heated at 35 °C for 30 min. It was then poured into a flask containing deionized water (50 mL) and further heated at 70 °C for 15 min. The mixture was then decanted into 250 mL of deionized water and the unreacted KMnO\(_4\) was removed by adding 3% hydrogen peroxide, H\(_2\)O\(_2\). The reaction mixture was then allowed to settle and decanted. The obtained graphite oxide was purified by repeated centrifugation and redispersed in deionized water until a neutralized pH was achieved. Finally, the resulting GO was dried at 60 °C in a vacuum oven for 48 h before use.

Preparation of reduced graphene oxide (rGO)\(^2\)

The reduction of GO was performed using a mixture of Hydriodic acid (55%)/Acetic acid (HI/AcOH). In detail, the as prepared GO powder (0.1 g) was sonicated in AcOH (37 mL) for 2 h. HI (2 ml) was then added and the mixture was stirred at 40 °C for 40 h. After being isolated by filtration, the product was washed through a three step procedure using saturated sodium bicarbonate, NaHCO\(_3\) (3×2.5 mL), distilled water (3×2.5 mL) and acetone (2×2.5 mL). Finally, the resulting rGO was dried at 60 °C in a vacuum oven overnight.

The reduction degree of the prepared rGO was characterized by X-ray photoelectron spectroscopy (XPS). Figure S1 shows the XPS C1s spectra of GO and rGO. The peaks for GO clearly indicate a substantial degree of oxidation with four components corresponding to carbon atoms in different functional groups: the non-oxygenated C at ~285 eV (C=C/C-C), the hydroxyl/epoxy groups at ~286.5 eV (C-OH/C-O), the carbonyl groups at ~288 eV (C=O), and the carboxylate carbon at ~289 eV (O=C-OH).\(^3\) XPS analysis revealed that a significantly larger proportion of oxygen in GO existed in the form of hydroxyl/epoxy groups.
and fewer proportion of oxygen was associated with C=O and O=C-OH functionalities. Compared to GO, the rGO C1s spectrum clearly exhibited much smaller related to oxygen peaks, indicating an efficient restoration of the sp² C-C bonds.

**Figure S1.** High-resolution XPS C1s spectra for (a) GO and (b) rGO.

Cyclic voltammetry (CV) was used to calculate the energy levels of rGO. The measurements were conducted in a three electrode apparatus, using a Pt foil as the counter electrode, a Pt disk as the working and a Ag/AgCl electrode as the reference one. The voltammetric behaviors of rGO in acetonitrile (CH₃CN) using 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF6) as the electrolyte at a scan rate of 10 mVs⁻¹ are demonstrated in **Figure S2**. The bands were calculated upon the formulas:⁴

\[
E_{\text{HOMO}} = -(E_{\text{onset}}^{\text{ox vs Fc/Fc}^+} + 5.1)(\text{eV})
\]

\[
E_{\text{LUMO}} = -(E_{\text{onset}}^{\text{ox vs Fc/Fc}^+} + 5.1)(\text{eV})
\]

The rGO HOMO level is approximately -4.96 eV calculated from the oxidation peak onset (0.32 V), while its LUMO level extracted from the onset of the reduction peak (-0.69 V) is -3.95 eV, consistent with previous results.⁵

**Figure S2.** Cyclic voltammetry curve of rGO, in CH₃CN using 0.1 M Tetrabutylammonium hexafluorophosphate (TBAPF6) as the electrolyte, at a scan rate of 10 mVs⁻¹. Inset demonstrates the reduction peak onset of rGO.

**Device fabrication.**

A FTO NSG 10 used as substrate was cleaned in 2% Hellmanex water solution by sonication. And then rinsed, first in water and finally in ethanol and acetone. A hole blocking layer of TiO₂ was deposited on the cleaned FTO by using spray pyrolysis at 450°C. The precursor spray solution was prepared by diluting titanium diisopropropoxide (30% in isopropanol) in ethanol by the proportions 5:95 by volume. Oxygen was used as a carrier gas. After spraying
the FTO was cooled to room temperature. On top of the compact TiO$_2$ layer, a mesoporous layer of TiO$_2$ nanoparticles was spin-coated at 2000 rpm for 10 s. TiO$_2$ paste (Dyesol 30 NR-D) was diluted in ethanol at a concentration of 125 mg/mL and used for mesoporous layer. Then substrates were sintered at on a hot plate for 30 minutes and then slowly cooled down.

For a lithium doping on TiO$_2$ layer, the substrates were re-heated to 450ºC and stayed for 30min after spin coating a 0.1 M Lithium bistrifluoromethanesulfonimidate, Li-TFSI, in acetonitrile at 3000 rpm for 10 s. After cooled down they were transferred directly into a nitrogen glovebox.

Perovskite solution was spin-coated in a glove box. The (FAPbI$_3$)$_{0.85}$(MAPbBr$_3$)$_{0.15}$ precursor solution was composed of FAI (1 M), PbI$_2$ (1.1 M), MABr (0.2 M) and PbBr$_2$ (0.2 M) in anhydrous DMF:DMSO 4:1 (v:v). This composition contains a lead excess as reported previously. The solution was spin-coated at 1000 rpm for 10 s and continuously at 6000 rpm for 30 s. During the second step, when approximately 15 seconds left before finish, 100 µL of anhydrous chlorobenzene was poured. After spin-coating, the films were annealed on a hotplate at 100°C for 90 min.

If the perovskite films were cooled to ambient temperature, a 70 mM solution of Spiro-OMeTAD dissolved in chlorobenzene was spin-coated on top of the films at 4000 rpm for 20 s. To doped Spiro-OMeTAD, three different additives were added 4-tert-butylypyridine, Li-TFSI in acetonitrile, and Co[t-BuPyPz]$_3$[TFSI]$_3$ (FK209) in acetonitrile. The molar ratio of Spiro:FK209:Li-TFSI:TBP was 1:0.03:0.5:3.3.

In this experiment, a concentration of rGO added to spiro-OMeTAD solution and perovskite solution is limited to 0.055mg/ml and 0.01µg/ml, respectively because rGO has a limited solubility on each solvent. In a mixed solvent of DMF:DMSO for perovskite solution and a chloro benzene for HTM solution these concentrations showed no precipitate after sonication for 2h. In case of TiO$_2$ solution, we chose the concentration when a maximum efficiency was obtained from an incorporation of rGO in the mesoporous TiO$_2$ layer.

Lastly, the 70 nm thick gold counter electrode was deposited by thermal evaporation.

**Solar cell Characterization**

The solar cells were characterized using a 450 W xenon light source (Oriel) equipped with a Keithley 2400 source meter. The light intensity was measured by a certified reference Si cell equipped with an IR-cutoff filter, KG5 (Newport), and it was adjusted to 1000W/m$^2$ during each measurement. A black metal mask of 0.16 cm$^2$ was used to fix the active area of the solar cells. A ZEISS Merlin high-resolution scanning electron microscope (HR-SEM) was performed for the morphology of the device cross-section and surface of films. X-ray powder diffractions were recorded on an D8 advance (Brucker) equipped with a ceramic tube (Cu anode, $\lambda = 1.54060$ Å) in an angle range of 20 = 10º to 70º.

**Photoluminescence (PL) Experiment**

Steady state PL spectra have been recorded using a spectrophotometer (Gilden Photonics) equipped with a cw Xenon lamp utilized as excitation. To detect the time resolved-PL trace a pulsed source at 460 nm (Ps diode lasers BDS-SM, pulse with < 100 ps, from Photonic Solutions, approx. 1mW power, 20MHz repetition rate, approx. 500 um spot radius) is used as excitation and the signal is recorded at 770 nm by the Time Correlated Single Photon
Counting detection technique with a time resolution of 1 ns. Excitation density of ~10 nJ/cm². All the samples have been encapsulated to prevent degradation or any oxygen/moisture induced effects. A monoexponential and bi-exponential fitting are used to analyze the background-corrected PL decay signal.

Figure S3. Cross-sectional field emission scanning electron microscopy (FESEM) of a) mp-TiO₂, b) rGO/mp-TiO₂, c) rGO/(FAPbI₃)₀.₈₅(MAPbBr₃)₀.₁₅, d) rGO/spiro-OMeTAD based perovskite solar cell.

Figure S4. The schematic image for energy level alignment of the materials used in our devices and the assumed recombination mechanism in the a) perovskite and b) spiro HTM layer.
Figure S5. PL spectra of the m-TiO$_2$ based sample treated with Li and with rGO in the TiO$_2$ matrix. To quantify the PL quenching due to electron transfer we measured the same sample upon excitation from the capping layer or from the TiO$_2$ layer. A quenching of about 45% is found.

Figure S6. PL decay upon excitation from the capping side at 460 nm. Sample 1. Perovskite/m-TiO$_2$; 2. Perovskite/m-TiO$_2$+Li; 3. Perovskite/rGO+m-TiO$_2$; 4. Perovskite/rGO+m-TiO$_2$+Li. Excitation density of ~10 nJ/cm$^2$. All the samples have been encapsulated to prevent degradation or any oxygen/moisture induced effects. The PL shows a monoexponential decay with a time constant beyond our temporal window. No difference is
observed among the samples investigated, because we are mainly probing the properties of the capping layer side that are similar in all the cases.

Table S1. PL fitting parameters for the time decay in Fig. 3b.

<table>
<thead>
<tr>
<th>Sample</th>
<th>A1 (%)</th>
<th>A2 (%)</th>
<th>τ1 (ns)</th>
<th>τ2 (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-TiO2</td>
<td>100</td>
<td></td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>m-TiO2+Li</td>
<td>47</td>
<td>53</td>
<td>1</td>
<td>22</td>
</tr>
<tr>
<td>m-TiO2+ rGO</td>
<td>100</td>
<td></td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>m-TiO2+Li+rGO</td>
<td>33</td>
<td>67</td>
<td>3</td>
<td>17</td>
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