

## Stable Perovskite Solar Cells Using Reduced Graphene Oxide Additive

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### Abstract

*Reduced graphene oxide (RGO) has been commonly used as an additive in the optoelectronic devices account to its unique properties. Here, we added 6% of RGO into mesoporous titanium dioxide (mp-TiO<sub>2</sub>) to improve the performance of perovskite solar cells (PSCs). The RGO addition resulting in enhanced the crystal structure and optical absorbance of the corresponding perovskite film. The charge transport also was improved and recombination processes reduced due to better interfacial perovskite/mp-TiO<sub>2</sub> contact. With this treatment, the optimized PSC achieved a power conversion efficiency of 14%. Most important, the humid long-term stability was improved after using RGO additive. PSCs with RGO maintained about 90% of their original performance after storage in ambient air with a relative humidity of 30-50%.*

**Key-words:** Perovskite, Reduced Graphene Oxide, Titanium Dioxide, Stability.

### 1. Introduction

As a result of population expansion and industrial development, global energy depletion has risen, putting renewable energy sources at risk of becoming unsustainable in the long term [1-5]. Environmental effect, cost, and efficiency of renewable energy generation are all factors that must be considered in the production of renewable energy [6-10]. Using photovoltaic (PV) systems to collect energy directly from the sun, on a global and really tiny scale, however, offers potential for producing energy both globally and locally [11]. Perovskite solar cells (PSCs) are a new class of solar cells that have a conventional cubic structure. It was described as having the general chemical formula: ABX<sub>3</sub>, where A stands for organic cation, and the most commonly used organic cations are methylammonium (MA), formamidinium (FA), and cesium (CS), among others [12]. The letters B and X represent inorganic (metallic) elements such as lead (Pb) and tin (Sn), respectively, whereas the letter X represent halide-based materials such as chloride (Cl), bromide (Br), and iodide (I). In

addition to having good characteristics such as an adjustable bandgap, a better optical absorption coefficient, a long charge diffusion time, and a high charge carrier mobility, perovskites also have excellent properties [13]. PV solar cell manufacturers have said that they would develop the third generation of solar cells since the power conversion efficiency (PCE) has risen from 3.8 percent to 25.2 percent since 2009 [14, 15].

It was the old one with poor efficiency and thermal and air stability [16, 17], and it was one of the three kinds of perovskite cation. The single cation methylammonium lead halide  $\text{CH}_3\text{NH}_3\text{PbI}_3$  (MAPbI<sub>3</sub>) was the other. The second kind of lead halide is a double cation formamidinium-methylammonium lead halide  $\text{CH}(\text{NH}_2)_2$ ,  $\text{CH}_3\text{NH}_3\text{PbI}_3$  (MAFAPbI<sub>3</sub>), which has a high PCE but is less stable than MAPbI<sub>3</sub>. MAPbI<sub>3</sub> has a high PCE but is less stable than MAFAPbI<sub>3</sub>. The final triple cation  $\text{CsFAMAPbI}_3$  perovskite, in which Cs is utilized to further enhance MA/FA perovskite compounds, has good thermal stability and high PCE [18, 19], whereas the first two materials exhibit excellent thermal stability and low PCE. Nanoparticles are particulate materials with at least one dimension of less than 100 nanometers in size, and they are defined as follows: Light can be manipulated and energy flow can be controlled at the atomic level using nanomaterials. [20]. Nanostructured solar cells, also known as nanowire solar cells, mesoscopic solar cells, and quantum dot solar cells, are a type of third- or next-generation solar cell that is based on nanostructures or nanostructured interfaces. Nanostructured solar cells have the potential to generate significant amounts of electricity. [21]. they hold a great deal of promise for developing novel methods of converting solar energy into electricity or thermal energy (in PV devices). Graphene is a carbon substance with a hexagonal structure similar to that of a honeycomb lattice and a thickness of 0.34 nm [22]. PSCs have made extensive use of graphene and graphene-based hybrid nanostructures due to their outstanding properties, which include high thermal and chemical stability, high electrical conductivity, high charge mobility, and low cost of fabrication. Graphene and graphene-based hybrid nanostructures have also been used in solar cells. [23]. Reduced graphene oxide (rGO) has excellent chemical and mechanical stability, as well as strong thermal conductivity and optical characteristics that are ideal for a variety of applications [24]. Chemical functionalization may readily modify these features. Because of the extraordinary characteristics of rGO, it has the potential to be a promising dopant for the electron transport layer (ETL) in order to improve the efficiency of PSCs.

In this work, we combined a triple-cation perovskite layer with  $\text{TiO}_2$ /RGO/ ETL, and we systemically explored the impacts of rGO additive in terms of performance, stability, the morphology of perovskite film, recombination process, and electrical properties. As a result, PSCs with a structure of FTO/c-TiO<sub>2</sub>/mp-TiO<sub>2</sub>/perovskite/Spiro-OMeTAD/Au demonstrated higher efficiency (14%) with

a higher reproducibility than those of the control devices without additive. Moreover, the modified PSCs revealed highly desirable ambient stability compared with the reference devices.

## 2. Experimental

To prepare the FTO (12  $\Omega$ /sq, Solaronix) glasses, they were sonicated with water, ethanol, and isopropanol s for 12 min. Then, the glasses were heated 15 min for drying. The hole-blocking TiO<sub>2</sub> (c-TiO<sub>2</sub>) films were prepared with spin-coating of a middle acid solution of titanium isopropoxide with a speed of 3000 rpm for 40 s. Then, the pure mp-TiO<sub>2</sub> (mp-TiO<sub>2</sub>) or RGO modified mp-TiO<sub>2</sub> layers were spin-coated above c-TiO<sub>2</sub> layers with a speed of 4000 rpm for 30 s. Both c-TiO<sub>2</sub> and mp-TiO<sub>2</sub> layers were baked at 500 °C for 1 h. The PVK film was fabricated as follows. First, a mixed solution of PbI<sub>2</sub> (600 mg, Alfa Aesar) and lead bromide (15 mg, Merck) in DMF (950  $\mu$ L) contains 10% CsPbI<sub>3</sub> in a volume ratio was spin-coated on FTO/c-TiO<sub>2</sub>/mp-TiO<sub>2</sub> substrates at 1500 rpm for 30 s, followed by annealing at 70 °C for 1 min. Then, a mixture of formamidinium iodide (FAI), methylammonium bromide (MABr), and methylammonium chloride (MACl) solution (60 mg/6 mg/6 mg) in IPA was poured on the PbI<sub>2</sub> layer, followed by spin coating at 1300 rpm for 30 s. To complete perovskite film fabrication, they were annealed at 150 °C for 15 min. The HTL mixture was obtained by adding 17.5  $\mu$ L of bis- (trifluoromethane) sulfonimide lithium salt (99.95%, Merck) in acetonitrile (Sigma-Aldrich, 520 mg/mL) and 28.8  $\mu$ L of 4- tertbutylpyridine (Merck, 97%) to 60 mM Spiro-OMeTAD in DCB. The HTL solution was deposited at 3000 rpm for 40 s on top of the perovskite film to develop the HTL film. Then, a 100 nm Au contact layer was sputtered on the HTL.

## 3. Results and Discussion

The morphologies of the perovskite films were studied using SEM images (Figure 1). As shown, by adding RGO, an appropriate perovskite film could be fabricated for solar cell applications compared to pure mp-TiO<sub>2</sub> based perovskite. The pinholes and grain boundaries (GBs) of the perovskite were minimized, they were unsuitable for PSCs since they served as charge recombination sites. The density of trap state between the GBs might be reduced using this modification strategy, enhancing the recombination processes' suppression and promoting the PSC's efficiency, which agrees well with the results of PL and I-V tests.

Figure 1 - FESEM images of perovskite films were deposited on mp-TiO<sub>2</sub> with (a) 0% and (b) 4% RGO modified mp-TiO<sub>2</sub>

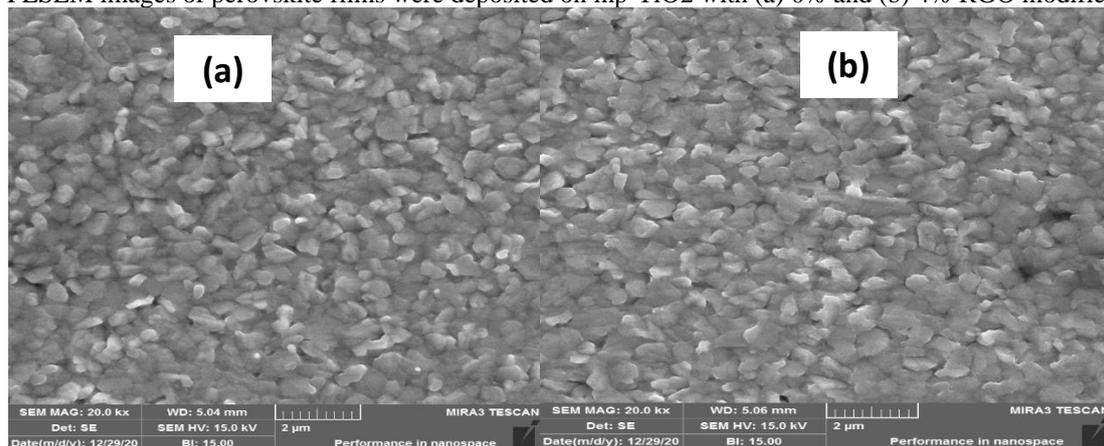
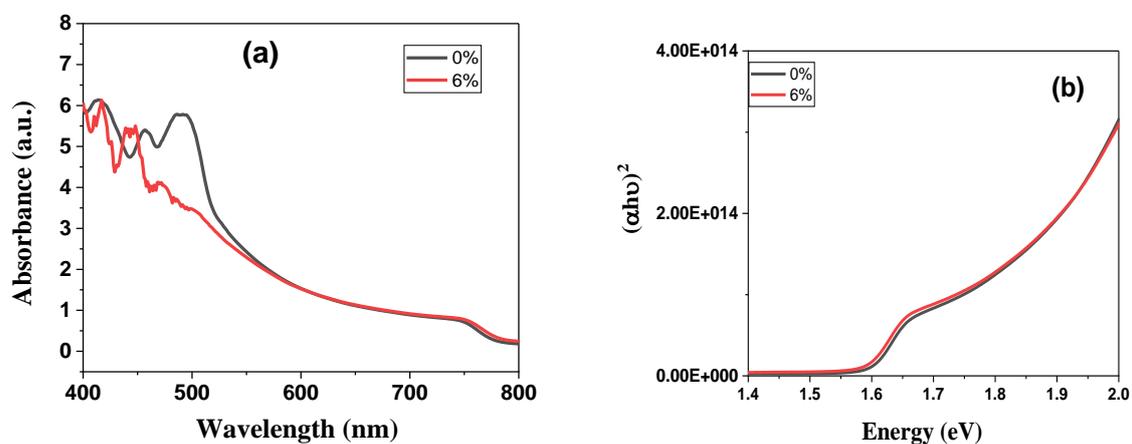


Figure 2a reveals the UV-vis spectra of the perovskite films deposited on mp-TiO<sub>2</sub> ETLs. An incorporating of the 6% RGO would result in a remarkable enhancement in the absorbance perovskite film within the visible wavelength. As we can see, the RGO nanocomposite did not affect the absorption edge of the perovskite. Also, the Tauc plots of perovskite films are shown in. Figure 2b. The plots demonstrate identical values of the bandgap energy ( $E_g$ ) about 1.58 eV. This resemblance was also seen in the perovskites' steady-state PL measurements.

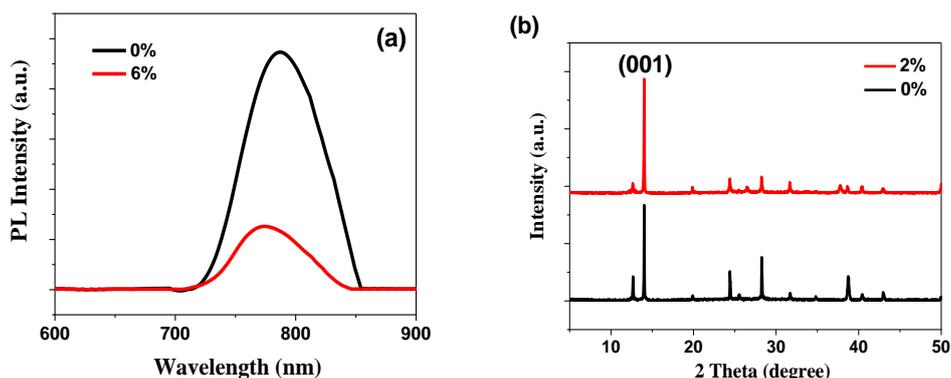
Figure 2 - (a) UV-vis absorption spectra and (b) corresponding Tauc plots of perovskite films deposited on 0% and 6% RGO additives.



The steady-state PL spectra are illustrated in Figure 3a. As clearly seen, the introducing rGO/Bi<sub>2</sub>O<sub>3</sub> additive produces the quenching of the PL peak, which indicates a more effective carrier's injection in the corresponding perovskites with less recombination rates. Figure 3b shows the XRD patterns of perovskites deposited on mp-TiO<sub>2</sub> ETMs. With the addition of the 2% rGO/Bi<sub>2</sub>O<sub>3</sub> additive, X-ray spectrum show that the main (001) signal was intensified, results in

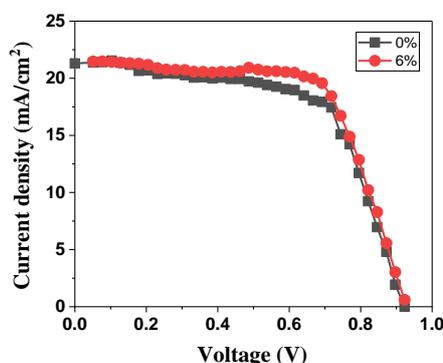
improved perovskite crystalline nature. The PbI<sub>2</sub> peak at 12.57°, which is unappreciated for PSCs. By using rGO/Bi<sub>2</sub>O<sub>3</sub>, this peak was drastically suppressed, implying resistance to humid degradation. The abovementioned measurements reveal that an addition the rGO/Bi<sub>2</sub>O<sub>3</sub> provides better ETM features and better perovskite quality.

Figure 3 - (a) Steady-state PL spectra and (b) XRD patterns of perovskite films deposited on 0% and 6% RGO additives.



The J-V plots are shown in Figure 4. Encouragingly, PSCs using RGO modified ETL revealed the PCE improvement by 26% relative to unmodified cells using a pure ETL. The representative PV parameters of the PSC with 2% rGO/Bi<sub>2</sub>O<sub>3</sub> demonstrated an Voc of 0.88 V, a Jsc of 21.6 mA cm<sup>-2</sup>, a FF of 70.2%, and a PCE of 14 %, while the control PSC showed a Voc of 0.88 V, a Jsc of 20.7 mA cm<sup>-2</sup>, a FF of 63.1%, and PCE of 12.2%. This improvement could originate from the electrically conducting merits of RGO and the low potential of carrier traps, where rGO additives could serve as an electron acceptor. As reported in the literature, the higher Voc achieved in the modified PSCs is because of the lower trap density in them and the suppressed recombination processes, which resulted from better energy level alignment between TiO<sub>2</sub> and perovskite film.

Figure 4 - J-V measurements of perovskite solar cells deposited on 0% and 6% RGO additives.



## 4. Conclusions

We present a novel RGO additive for the construction of high-performance mesoporous PSCs in a nutshell. As an electron acceptor/transport mediator ETLs, this technique employs a nanocomposite structure of RGO that is incorporated into mp-TiO<sub>2</sub>. RGO-based PSCs exhibit better charge injection and less recombination than control PSCs, which results in higher J<sub>sc</sub> and PCE. Our results indicate that rGO may be a useful additive in PSCs. As a consequence, the PV parameters of the PSCs have improved. Importantly, the RGO additive achieves a champion PCE of 14 percent.

## References

- A. K. Al-Mousoi and M. K. Mohammed, "Engineered surface properties of MAPI using different antisolvents for hole transport layer-free perovskite solar cell (HTL-free PSC)," *Journal of Sol-Gel Science and Technology*, vol. 96, no. 3, pp. 659-668, 2020.
- G. A. Al-Dainy, S. E. Bourdo, V. Saini, B. C. Berry, and A. S. Biris, "Hybrid Perovskite Photovoltaic Devices: Properties, Architecture, and Fabrication Methods," *Energy Technology*, vol. 5, no. 3, pp. 373-401, 2017.
- Q. A. Akkerman and L. Manna, "What Defines a Halide Perovskite?," *ACS Energy Letters*, vol. 5, no. 2, pp. 604-610, 2020.
- P. Gao, M. Grätzel, and M. K. Nazeeruddin, "Organohalide lead perovskites for photovoltaic applications," *Energy & Environmental Science*, vol. 7, no. 8, pp. 2448-2463, 2014.
- Y. Y. Choo, "Development and Characterisation of Perovskite Solar Cells," *Monash University*, 2020.
- W.-G. Li, H.-S. Rao, B.-X. Chen, X.-D. Wang, and D.-B. Kuang, "A formamidinium-methylammonium lead iodide perovskite single crystal exhibiting exceptional optoelectronic properties and long-term stability," *Journal of Materials Chemistry A*, vol. 5, no. 36, pp. 19431-19438, 2017.
- M. Saliba et al., "Cesium-containing triple cation perovskite solar cells: improved stability, reproducibility and high efficiency," *Energy & environmental science*, vol. 9, no. 6, pp. 1989-1997, 2016.
- P. Christian, F. Von der Kammer, M. Baalousha, and T. Hofmann, "Nanoparticles: structure, properties, preparation and behaviour in environmental media," *Ecotoxicology*, vol. 17, no. 5, pp. 326-343, 2008.
- A. Barhoum and A. S. H. Makhlouf, *Emerging Applications of Nanoparticles and Architecture Nanostructures*. Elsevier, 2018.
- F. Alussail, *Synthesis and Characterization of Reduced Graphene Oxide Films*, University of Waterloo, 2015.
- N. Balis et al., "Investigating the role of reduced graphene oxide as a universal additive in planar perovskite solar cells," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 386, p. 112141, 2020.

- J. V. Milić, N. Arora, M. I. Dar, S. M. Zakeeruddin, and M. Grätzel, "Reduced graphene oxide as a stabilizing agent in perovskite solar cells," *Advanced Materials Interfaces*, vol. 5, no. 22, p. 1800416, 2018.
- M. Batmunkh, C. J. Shearer, M. J. Biggs, and J. G. Shapter, "Nanocarbons for mesoscopic perovskite solar cells," *Journal of Materials Chemistry A*, vol. 3, no. 17, pp. 9020-9031, 2015.
- H.-S. Kim et al., "Reduced graphene oxide improves moisture and thermal stability of perovskite solar cells," *Cell Reports Physical Science*, vol. 1, no. 5, p. 100053, 2020.
- M. Ghasemi et al., "Phenethylammonium bismuth halides: from single crystals to bulky-organic cation promoted thin-film deposition for potential optoelectronic applications," *Journal of Materials Chemistry A*, vol. 7, no. 36, pp. 20733-20741, 2019.
- C. Lan et al., "Lead-free formamidinium bismuth perovskites (FA) 3Bi2I9 with low bandgap for potential photovoltaic application," *Solar Energy*, vol. 177, pp. 501-507, 2019.
- K. Ahmad, "Bismuth Halide Perovskites for Photovoltaic Applications," *In Bismuth-Fundamentals and Photonic Applications: IntechOpen*, 2020.
- O. Üner, N. Aslan, A. Sarioğlu, F. Semerci, and M. M. Koc, "Facile Preparation of Commercial Bi2O3 Nanoparticle Decorated Activated Carbon for Pseudocapacitive Supercapacitor Applications," 2021.
- N. C. Miller and M. Bernechea, "Research Update: Bismuth based materials for photovoltaics," *APL Materials*, vol. 6, no. 8, p. 084503, 2018.
- S. Wu et al., "A chemically inert bismuth interlayer enhances long-term stability of inverted perovskite solar cells," *Nature communications*, vol. 10, no. 1, pp. 1-11, 2019.
- T. Umeyama et al., "Boosting of the performance of perovskite solar cells through systematic introduction of reduced graphene oxide in TiO2 layers," *Chemistry Letters*, vol. 44, no. 10, pp. 1410-1412, 2015.
- G. S. Han et al., "Reduced graphene oxide/mesoporous TiO2 nanocomposite based perovskite solar cells," *ACS applied materials & interfaces*, vol. 7, no. 42, pp. 23521-23526, 2015.
- K. T. Cho et al., "Beneficial role of reduced graphene oxide for electron extraction in highly efficient perovskite solar cells," *ChemSusChem*, vol. 9, no. ARTICLE, pp. 3040-3044, 2016.
- M. M. Tavakoli, R. Tavakoli, S. Hasanzadeh, and M. H. Mirfasih, "Interface engineering of perovskite solar cell using a reduced-graphene scaffold," *The Journal of Physical Chemistry C*, vol. 120, no. 35, pp. 19531-19536, 2016.