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Stable and durable CH$_3$NH$_3$PbI$_3$ perovskite solar cells at ambient conditions

Nagalingam Rajamanickam$^{1,3,4}$, Sudesh Kumari$^{1,4}$, Venkat Kalyan Vendra$^{1,2,4}$, Brandon W Lavery$^{1,2}$, Joshua Spurgeon$^1$, Thad Druffel$^1$ and Mahendra K Sunkara$^{1,2}$

$^1$ Conn Center for Renewable Energy Research, University of Louisville, Louisville, KY 40292, USA
$^2$ Department of Chemical Engineering, University of Louisville, Louisville, KY 40292, USA
$^3$ School of Physics, Madurai Kamaraj University, Madurai 625021, Tamil Nadu, India

E-mail: mahendra@louisville.edu

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Abstract

Degradation of metal–organic halide perovskites when exposed to ambient conditions is a crucial issue that needs to be addressed for commercial viability of perovskite solar cells (PSCs). Here, a concept of encapsulating CH$_3$NH$_3$PbI$_3$ perovskite crystals with a multi-functional graphene–polyaniline (PANI) composite coating to protect the perovskite against degradation from moisture, oxygen and UV light is presented. Hole-conducting polymers containing 2D layered sheet materials are presented here as multi-functional materials with oxygen and moisture impermeability. Specific studies involving PANI and graphene composites as coatings for perovskite crystals exhibited resistance to moisture and oxygen under continued exposure to UV and visible light. Most importantly, no perovskite degradation was observed even after 96 h of exposure of the PSCs to extremely high humidity (99% relative humidity). Our observations and results on perovskite protection with graphene/conducting polymer composites open up opportunities for glove-box-free and atmospheric processing of PSCs.

Keywords: perovskite, composite coating, moisture stability, oxygen stability, graphene–polyaniline composite

(Some figures may appear in colour only in the online journal)

Introduction

Perovskite based solar cells have garnered significant interest due to the attractive properties of metal–organic halide perovskites such as high electron and hole diffusion lengths [36, 40], high absorption coefficients [27], and ambipolar charge (electron and hole) transport [16]. State-of-the-art lab scale CH$_3$NH$_3$PbI$_3$ solar cells prepared in a humidity controlled glove box have reached power conversion efficiencies of ~20% surpassing the best performing dye-sensitized and amorphous Si solar cells [11, 19]. Efficiency improvements of CH$_3$NH$_3$PbI$_3$ perovskite solar cells (PSCs) over the past few years have been achieved using different anode architectures [12, 20, 31], deposition methods [8, 21, 25, 30, 39], different halides and organic cations in the perovskite structure [2, 22, 35], and improved electron and hole transport materials (HTMs) [3, 13]. In spite of this tremendous progress, a number of key issues must be overcome before commercialization is possible; mainly the long term stability of the CH$_3$NH$_3$PbI$_3$ material in the presence of water, UV irradiation, and O$_2$. Grätzel et al reported that the device fabrication...
should be carried out under controlled atmospheric conditions and with a relative humidity (RH) of <1% for achieving consistent results and high efficiencies [4].

The degradation mechanisms of CH$_3$NH$_3$PbI$_3$ PSCs in the presence of moisture, air and UV are summarized in figure 1. In the presence of significant moisture, the CH$_3$NH$_3$PbI$_3$ degrades into the original PbI$_2$ and CH$_3$NH$_3$I. The degradation reaction is initiated when a water molecule interacts with the proton present in the CH$_3$NH$_3$PbI$_3$ crystal and ultimately degrades to form aqueous HI, solid PbI$_2$, and volatile CH$_3$NH$_2$. The degradation route for CH$_3$NH$_3$PbI$_3$ sample in the presence of UV and O$_2$ is shown in figure 1(b) [1, 28]. In the case of oxygen, it is thought that a superoxide is generated through an electron transfer from the photoexcited CH$_3$NH$_3$PbI$_3$ to an O$_2$ molecule. The resulting superoxide chemically attacks the perovskite absorber and decomposes it to PbI$_2$ and other precursors.

A number of reports have addressed the issue of degradation of the perovskite material due to moisture [4, 26]. These studies include use of hydrophobic HTMs [41], fabricating layered perovskites, and using alumina coatings on the surface of the perovskite [24, 26]. However, none of these approaches completely prevent the percolation of moisture through the films and ultimately still result in perovskite deterioration. Moreover, the stability of these coatings has only been evaluated in low to moderate humidity (20%–60% RH). The use of insulating Al$_2$O$_3$ as a protective coating strictly requires the use of an extremely thin layer so as not to inhibit charge-transfer, which limits the functionality as an impermeable barrier to moisture. After 18 h of testing at 60% RH, Niu et al observed that the power conversion efficiency of Al$_2$O$_3$ dip-coated PSCs dropped by half from 4.6% to 2.1% [26].

Relatively few studies explore the stability of perovskite solar cells against ultra-violet irradiation and oxygen [23]. Aristidou et al investigated the influence of light and oxygen on the stability of CH$_3$NH$_3$PbI$_3$ perovskite based photoactive layers. According to their observation, the degradation is initiated by the reaction of superoxide (O$_2^-$) with the methylammonium moiety of the CH$_3$NH$_3$PbI$_3$ perovskite absorber [1]. Chander et al reported a method involving a spray coated transparent layer of down-shifting YVO$_4$:Eu$^{3+}$ nano-
phosphor layer to absorb UV light [6]. In another study, Sb$_2$S$_3$ layers were inserted between the TiO$_2$ and CH$_3$NH$_3$PbI$_3$ used to protect the CH$_3$NH$_3$PbI$_3$ solar cells against the degradation due to light exposure [18]. Studies on lead free organic–inorganic halide perovskites such methyl ammonium tin iodide reported that these materials are both oxygen and moisture sensitive [15]. Hence, oxygen impermeability is also a critical factor that needs to be considered when designing a protective coating for the CH$_3$NH$_3$PbI$_3$ devices. However, none of these reports studied the effect of moisture on their respective perovskite devices. As shown in figure 1, even the trace of moisture or air and UV is detrimental to the performance of the CH$_3$NH$_3$PbI$_3$ solar cell.

An ideal protective coating encapsulating the CH$_3$NH$_3$PbI$_3$ should not only be impermeable to moisture but also to oxygen as well. Composites comprising of layered silicates or clays dispersed in a polymeric matrix have been extensively investigated as barrier materials for oxygen and water because of the increase in tortuosity of the path of the molecule diffusing through the coating [9, 29]. Moisture and oxygen resistant materials that are also highly conductive can be rationally designed and developed as protective coating layers. When a polymeric composite is used as a protective coating, it is essential to have higher thickness to increase the tortuosity in the path of gas and water molecules. Hence, it becomes important to choose components that have high electron and hole conductivity besides having good barrier properties to gases and water, so that the thickness of the coating does not impede charge-transfer and hinder photovoltaic performance. Defect-free multilayer graphene has been demonstrated to be impermeable to moisture and many gases due to small inter layer spacing [37]. Further, sub-micron-thick films of highly reduced graphene oxide have demonstrated two orders of magnitude higher moisture impermeability compared to aluminized polyethylene terephthalate used as an industrial standard [37]. The excellent gas and moisture barrier properties of graphene combined with its high electrical conductivity makes it a suitable disperse material in the composite. The use of graphene with a conductive polymer having excellent hole transport properties can act as an effective protective coating for the CH$_3$NH$_3$PbI$_3$ perovskite. The concept is schematically illustrated in figure 2. In this work, graphene and polyaniline (PANI) composite are used to show a proof-of-concept of the CH$_3$NH$_3$PbI$_3$ stability with composite coatings. Graphene/PANI composites are used as a protective coating in CH$_3$NH$_3$PbI$_3$ solar cells utilizing copper iodide (CuI) as a HTM. The graphene/PANI composite protects the CH$_3$NH$_3$PbI$_3$ from the detrimental effects of both moisture, and UV with oxygen. The composite serves as a better protective coating than either graphene or PANI alone. In addition, the high electrical conductivity of the graphene/PANI composites can enable the use of a thick coating to create a moisture-resistant seal around the CH$_3$NH$_3$PbI$_3$ while maintaining the photovoltaic performance.

**Results and discussion**

**Characterization of perovskite stability from x-ray diffraction (XRD) measurements**

The influence of moisture, UV and oxygen exposure on the stability of CH$_3$NH$_3$PbI$_3$ perovskite samples, with and without the graphene, or PANI, or graphene/PANI composite coatings, were analyzed using XRD. Figures 3(a) and (b) show the time evolution of the XRD patterns of the unprotected CH$_3$NH$_3$PbI$_3$ samples exposed to air having 99% RH. The crystallite size of the CH$_3$NH$_3$PbI$_3$ is 27 nm as calculated from the Scherrer formula. All the XRD peaks are indexed to a tetragonal perovskite structure having lattice constants of $a = b = 8.867$ Å and $c = 12.797$ Å, which is in agreement...
with earlier reports [2, 7, 12, 33]. The peak positions of methyl ammonium iodide and lead iodide are also shown for comparison. The intensity of the CH$_3$NH$_3$PbI$_3$ perovskite peaks decreased with increasing exposure times and the intensity of the lead iodide and iodine increased. The peaks at 12.66° and 52.34° can be indexed to (001) and (004) planes of hexagonal lead iodide (JCPDS #801000). The peak at 38.61° can be assigned to the (020) plane of orthorhombic iodine (JCPDS #792440). These peaks were not observed in the CH$_3$NH$_3$PbI$_3$ samples coated with the graphene/PANI composite (figure 3(c)), suggesting that composite coating effectively protects the CH$_3$NH$_3$PbI$_3$ from degradation against moisture. Thus, after moisture exposure, the unprotected CH$_3$NH$_3$PbI$_3$ samples turned yellow and exhibited less light absorption while the graphene/PANI CH$_3$NH$_3$PbI$_3$ still exhibited the characteristic black color of the CH$_3$NH$_3$PbI$_3$ (supporting information figures S1 and S2).

XRD measurements were also performed on the CH$_3$NH$_3$PbI$_3$ crystals coated with graphene/PANI composite, or graphene, or PANI (for procedure refer to the methods section). Figure 4 shows the XRD data after exposure to air with 99% RH for 2 days. XRD patterns of PbI$_2$ and CH$_3$NH$_3$PbI$_3$ crystals (made in situ) are shown as 4(a) and (b), respectively. The CH$_3$NH$_3$PbI$_3$ crystals with the graphene/PANI composite did not show any sign of degradation even after exposure to 99% RH for 2 days. The CH$_3$NH$_3$PbI$_3$ crystals coated with graphene showed XRD patterns similar to the graphene/PANI composite CH$_3$NH$_3$PbI$_3$ perovskite. However, there is an additional peak observed in figures 4(c) and (d) at 26.5° which is related to the pristine graphene sample used in the protective composite (figure S2). On the other hand, the CH$_3$NH$_3$PbI$_3$ with PANI alone shows an intense peak at 12.6° indicating complete degradation of CH$_3$NH$_3$PbI$_3$ sample into PbI$_2$.

In order to investigate the impact of O$_2$ and UV exposure on the CH$_3$NH$_3$PbI$_3$ crystals coated with graphene and/or PANI, time evolved XRD patterns are studied. The CH$_3$NH$_3$PbI$_3$ crystals coated with graphene or PANI were exposed to a UV lamp to expedite the degradation process. As shown in figures 5(e) and (f), the CH$_3$NH$_3$PbI$_3$ crystals with PANI coating showed significant degradation after 30 min of exposure and after 1 h of exposure there was no sign of the presence of CH$_3$NH$_3$PbI$_3$ crystals. The characteristic peak associated with PbI$_2$ was not observed in this case because the CH$_3$NH$_3$PbI$_3$ crystals are decomposed into various lead oxides. However, CH$_3$NH$_3$PbI$_3$ crystals coated with graphene did show better resistance towards the degradation caused by the presence of UV and O$_2$. The XRD pattern (figure 5(d)) of CH$_3$NH$_3$PbI$_3$ crystals coated with graphene after 1 h of exposure shows a significant presence of CH$_3$NH$_3$PbI$_3$ with some degradation into PbI$_2$ (peak at 12.6°).

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis of perovskite crystals

To understand the morphology of the perovskite crystals with the various protective coatings, TEM (figure 6) of CH$_3$NH$_3$PbI$_3$ crystals was performed. The CH$_3$NH$_3$PbI$_3$ crystal size ranges from 500 nm to 1000 nm. Figures 6(b) and (c) shows that the graphene/PANI composite forms a thick layer of about 5–50 nm on the CH$_3$NH$_3$PbI$_3$ crystals. Clearly,
TEM images (6(a)–(c)) of CH$_3$NH$_3$PbI$_3$ crystals with graphene/PANI composite shows that the crystals are fully encapsulated. On the other hand, CH$_3$NH$_3$PbI$_3$ crystals with graphene or PANI alone are covered with the respective coatings but due to inherent morphology of graphene and PANI, there are few areas that are exposed to ambient conditions. For example, due to the sheet like structure of graphene, the CH$_3$NH$_3$PbI$_3$ crystals are not completely covered (figures 6(d)–(f)). With PANI coating, the CH$_3$NH$_3$PbI$_3$ crystals are fully encapsulated but due to the porous nature of the PANI coating air can easily diffuse and can lead to the degradation of the CH$_3$NH$_3$PbI$_3$. These TEM images shows that graphene/PANI composite should form a better protective coating for the CH$_3$NH$_3$PbI$_3$ crystals compared to that of graphene and PANI alone which is consistent with the XRD patterns observed in figures 4 and 5. To validate if the graphene/PANI composite conformally coated the CH$_3$NH$_3$PbI$_3$ crystals, TEM analysis with elemental mapping was performed. Figure 7(a) depicts the TEM image of an unprotected CH$_3$NH$_3$PbI$_3$ crystal. Figure 7(b) shows the TEM image of a graphene/PANI composite coated CH$_3$NH$_3$PbI$_3$ crystal and clearly indicates that the composite forms a thick conformal layer on the CH$_3$NH$_3$PbI$_3$ crystals. Comparing the C–K and Pb–M, I–K, Ti–K elemental maps obtained from energy dispersive x-ray spectroscopy in the TEM (figure 7(c)), it can be concluded that the graphene/PANI composites uniformly encapsulate the CH$_3$NH$_3$PbI$_3$ crystals.

To investigate the morphology of graphene/PANI composite on the CH$_3$NH$_3$PbI$_3$ perovskite electrodes cross-section SEM images (figure 8) were also obtained. Cross-section SEM images revealed that the composite coating was infiltrated into the CH$_3$NH$_3$PbI$_3$/TiO$_2$ region of the solar cells and further formed a thick overlayer at the top. In this work, we were motivated to use copper iodide as a HTM because of the low cost (two orders of magnitude lower cost than Spiro-OMeTAD) and high commercial availability when compared with spiro-OMeTAD used in the best performing cells reported in literature [32]. In addition, to simplify the fabrication process, we sputtered gold on glass slide and sandwiched it with CH$_3$NH$_3$PbI$_3$ perovskite electrodes coated with the copper iodide as opposed to the conventional route of
thermally evaporating gold. A schematic of the device architecture is shown in figure 9(a). Figure 9(b) depicts the band edge positions of the different materials used in this work. Graphene present in the composite aids in the electronic transport, while PANI assists in the hole transport to copper iodide. From the photoluminescence measurements, a strong quenching with graphene/PANI protected CH$_3$NH$_3$PbI$_3$ sample has been observed, which implies possible charge transfer processes occurred at the protective coating and CH$_3$NH$_3$PbI$_3$ interface (figure S6). The sandwich approach followed in this paper could create opportunities for roll to roll or laminated CH$_3$NH$_3$PbI$_3$ cells, which could offer significant reduction in the processing costs.

Current density–voltage analysis

Current density–voltage (J–V) curves were obtained after exposing the CH$_3$NH$_3$PbI$_3$ solar cell to high humidity (99% RH) for different times. The unprotected CH$_3$NH$_3$PbI$_3$ cells showed a rapid decline in the short-circuit current density and open circuit-voltage (figure 10(a)) with time. After 1 h of exposure to moisture, no photovoltaic behavior is seen from the cells. Figures 10(b) and (d) shows the J–V curves of CH$_3$NH$_3$PbI$_3$ solar cells encapsulated with graphene/PANI composite, with different thickness of the overlayers. Increasing the overlayer thickness improved the stability of the cells to moisture. The CH$_3$NH$_3$PbI$_3$ solar cell with the thickest overlayer (≈4 μm) coating formed by spin coating the PANI and graphene solution four times (4x) showed little variation in the photovoltaic performance with time when continuously exposed to high humidity. Increasing the thickness of the composite, increases the tortuosity in the path that water molecules have to travel before they can reach the CH$_3$NH$_3$PbI$_3$ crystals. This explains why thicker overlayers of the composite coating show better stability in high humidity conditions. The best performing cell with a protective coating showed a photocurrent of 14 mA cm$^{-2}$ and an open-circuit voltage of 450 mV. The low open-circuit voltage observed when compared to the best performing cell in literature fabricated with spiro-OMeTAD is due to the high recombination losses with CuI [10]. The performance of the device can be further optimized by a HTM that exhibits lower recombination losses than copper iodide. Devices fabricated without CuI, utilizing graphene/PANI itself as the HTM showed higher open-circuit voltage of 0.8 V, but lower short-circuit current density of 2.6 mA cm$^{-2}$ due to low conductivity of PANI when compared with copper iodide (supporting information figure S6). Further optimization, involving the use of more conductive polymeric materials than PANI can also boost the efficiency of the devices. A variation in photocurrents is observed in samples with different overlayer thickness, this could be due to the graphene/PANI composite acting as a buffer layer and preventing the direct contact of TiO$_2$ and the copper iodide HTM. Lack of sufficient control over the crystal size during the CH$_3$NH$_3$PbI$_3$ growth is also another factor that can contribute to the variation of photocurrents and hence claims with regards to the increase in the photocurrents with the graphene/PANI encapsulating layer cannot be made [17]. Nevertheless, the results in figure 10 show that graphene/PANI composite can provide a leak tight seal for the CH$_3$NH$_3$PbI$_3$ against moisture and oxygen. Using the J–V data of the devices in figure 10, the shunt ($R_{SH}$) and series resistances ($R_S$) are calculated to analyze the effect of graphene/PANI protective coating on the electrical performance of the devices, as shown in table S5 (see supporting information). The degradation of the perovskite is caused by the diffusion of oxygen and moisture into the perovskite layer. Regardless of the shunt and series resistances of the cells, we expect the perovskite degradation mechanism to be the same. Hence, the results of the obtained with lower shunt and higher series resistances (when compared to best performing cells) could be extended to high efficiency cells. Further, to ensure proper comparison we made a reference cell without protective coating and compared our efficiencies.

The device without any graphene/PANI coating exhibited a 90 KΩ of $R_{SH}$ and a 49 KΩ of $R_S$. While the device with one graphene/PANI coating showed a decrease in both $R_{SH}$ and $R_S$ to a 65 and 37 KΩ, respectively; this trend continues with each new addition of the graphene/PANI coating. Although the $R_{SH}$ and $R_S$ resistances are decreasing with increase in number of graphene/PANI coatings, but the ratio of $R_{SH}/R_S$ has increased from 1.83 to 3.11 for the devices without graphene/PANI coating and with four graphene/PANI coatings. As discussed in the above section, the TEM analysis of the device with the graphene/PANI coating clearly showed graphene percolation in the CH$_3$NH$_3$PbI$_3$. Due to graphene percolation into the perovskite film, a more conductive nanocomposite is formed which results in a

![Figure 6](image_url)
decrease in the $R_S$ of the coated devices. At the same time, PANI/CuI might come in contact with the TiO$_2$, resulting in recombination between the conduction band electrons of TiO$_2$ and holes of PANI/CuI, and leading to the lower $R_{SH}$. Another possible reason for the decrease in the $R_{SH}$ could be the low conductivity of the updoped PANI compared to the CuI.$^{10,34}$ The increased tortuosity for the diffusion of water molecules result in an improved stability of the CH$_3$NH$_3$PbI$_3$. According to our calculations, $\sim 4\mu m$ thick coating of the graphene–polymer composite is sufficient to keep the water diffusion time scales as long as ten years (see supporting info). Interestingly, the redox potential of an aqueous O$_2$/O$_2^{-}\,$ is located below the LUMO of CH$_3$NH$_3$PbI$_3$ at 4.12 eV w.r.t vacuum level (or $-0.28$ V versus SHE) $^{14}$. The electron affinity of an O$_2$ molecule in gas phase is 0.45 eV, which is above the LUMO of CH$_3$NH$_3$PbI$_3$ $^{5}$. Therefore, superoxide radical can be formed by two pathways (a) in absence of moisture, a hot electron from CH$_3$NH$_3$PbI$_3$ created by a high energy UV photon can results in the formation of the superoxide radical which can lead to the degradation CH$_3$NH$_3$PbI$_3$ as shown in figure 1(b) in presence of moisture, as the conduction band electrons from CH$_3$NH$_3$PbI$_3$ generated due to the visible light absorption can reduce an oxygen molecule to superoxide radical. Of these two pathways, the second pathway leads to the formation of higher amounts of superoxide because of relatively higher fraction of visible light when compared to UV light in the solar spectrum. Hence protecting the CH$_3$NH$_3$PbI$_3$ from moisture can also suppress the superoxide radical formation by the second reaction pathway, resulting in improved oxygen stability.

In summary, graphene/PANI composite has been found to act as a multifunctional coating enabling charge-carrier transport while simultaneously providing an impermeable seal to moisture, demonstrating a proof-of-concept composite coating for enhanced photovoltaic stability. The composite prevents degradation of the CH$_3$NH$_3$PbI$_3$ from moisture, UV and air as shown by the constant short circuit current density over an extended period of time. The protective coating effectively prevents the deterioration of the CH$_3$NH$_3$PbI$_3$ into the PbI$_2$ and I$_2$. The high moisture impermeability could allow the processing of CH$_3$NH$_3$PbI$_3$ cells under atmospheric conditions once they are encapsulated with graphene/PANI composite. The use of composite protective coating developed in this work could also be extended to other lead free organic–inorganic metal halide perovskite that are both oxygen and moisture sensitive. The sandwich approach followed in this paper could create opportunities for roll to roll or laminated perovskite cells, which could offer significant reduction in the processing costs. Ongoing efforts involve fabrication of higher efficiency cells with spiro, optimization

Figure 7. TEM image of (a) unprotected CH$_3$NH$_3$PbI$_3$ crystal and (b) CH$_3$NH$_3$PbI$_3$ encapsulated graphene/PANI composite (c) EDS color map of the encapsulated CH$_3$NH$_3$PbI$_3$ in figure 7(b) indicating complete coverage of the CH$_3$NH$_3$PbI$_3$ crystal with the graphene/PANI composite.
of the composite coatings for the cells and the use of laminated counter electrode. The atmospheric roll to roll processing of CH$_3$NH$_3$PbI$_3$ solar cells using the moisture protected CH$_3$NH$_3$PbI$_3$ crystals using composite coatings described here is currently being pursued and will be reported later in a subsequent report. Similar concepts can also be applied to design and develop polymer materials for lamination to provide long-term-stability.

Methods

Perovskite crystals

CH$_3$NH$_3$PbI$_3$ crystals were synthesized from γ-butyrolactone (Sigma Aldrich) solution containing equimolar mixture of CH$_3$NH$_3$I and PbI$_2$. The concentration of the equimolar mixture of CH$_3$NH$_3$I and PbI$_2$ was kept at 40.26 wt%. The mixture in γ-butyrolactone was kept at 60°C with stirring overnight. Black shining CH$_3$NH$_3$PbI$_3$ crystals were formed by heating the solution at 220°C on a hot plate. For the humidity and UV/O$_2$ degradation measurements the CH$_3$NH$_3$PbI$_3$ crystals were mixed with graphene and PANI solutions. Graphene flakes and PANI were dissolved in 2-propanol in 1:10 and 2:5 weight ratio, respectively. After mixing the CH$_3$NH$_3$PbI$_3$ crystals with graphene and/or PANI, the solution was stirred for 1 h. For the measurements, few drops of the mixture were drop casted on a cleaned glass slide.

Substrate preparation

Fluorine doped tin oxide (FTO) coated substrates (Hartford glass, USA) were etched using zinc metal powder and 2 M hydrochloric acid. These etched substrates were cleaned by ultra-sonication in an alkaline, aqueous washing solution, rinsed with deionized water, and ethanol and subjected to oxygen plasma (PLAMAX 150S) treatment for 15 min.

CH$_3$NH$_3$PbI$_3$ synthesis and device fabrication

To deposit the TiO$_2$ compact layer, titanium diisopropanoate bis-acetylacetonate (TAA) was dissolved in 1-butanol and 0.15 M and 0.3 M solutions of TAA were prepared. The 0.15 M and 0.3 M (three times) TAA solutions were spin coated on the FTO substrates at 4000 rpm for 30 s followed by heated the substrates at 500°C for 30 min. After cooling to room temperature, the substrates
were immersed in a 40 mM aqueous solution of TiCl$_4$ for 30 min at 70 °C, rinsed with deionized water and heated at 500 °C for 30 min. The mesoporous TiO$_2$ layer was deposited by spin coating a commercial TiO$_2$ paste (Dyesol-18NRT, Dyesol) diluted in ethanol (1:3.5, weight ratio) at 5000 rpm for 30 s using. After drying at 125 °C, the TiO$_2$ films were gradually heated to 500 °C for 30 min and cooled to room temperature and TiCl$_4$ treatment was performed again on the substrates. The sequential deposition procedure developed by Graetzel and coworkers was used for the CH$_3$NH$_3$PbI$_3$ deposition discussed as follows was performed in an argon glove box and is detailed as follows. Solutions of graphene and PANI in 2-propanol are alternatively spin coated to form the composite coating. The procedure is repeated several times to build up the thickness of the composite layers. For instance, a 2× coating denotes that the alternate deposition of graphene and PANI was performed twice in an alternate fashion. Graphene flakes (Cheaptubes, USA) dissolved in 2-propanol (1:10, weight ratio) and the samples are dried for 80 °C for 10 min after spin coated at 2000 rpm for 10 s. Then PANI (Aldrich) was dissolved in 2-propanol (2:5, weight ratio) and spin coated at 2000 rpm for 10 s followed by drying at 80 °C for 10 min.

**Device fabrication**

The copper iodide (CuI) used as the HTM was then deposited by a doctor blade technique [38]. The CuI solution was prepared by dissolving 0.1 M of CuI in dipropyl sulfoxide (Sigma Aldrich). Following the deposition, the substrates dried at 70 °C–80 °C for 20 min after the doctor blading. The device fabrication was carried out under controlled atmospheric conditions and a humidity of <0.2%. Gold was deposited on separate glass plate by RF sputtering at 80 mTorr and 18 mV conditions for 4 min. The sputtered electrodes are mechanically pressed onto the copper iodide coated electrode to sandwich the two electrodes.

**Humidity testing**

The humidity measurements were done at 99% RH in glove box using a hygrometer (Omega HH314A). The high humidity was reached by heating the distilled water at constant temperature (∼54 °C).

**UV treatment**

For UV measurements CH$_3$NH$_3$PbI$_3$ samples were exposed to UV lamp (F600S UV lamp-H bulb) for different time intervals. After each hour the lamp was turned off for 5–10 min to avoid the heating of CH$_3$NH$_3$PbI$_3$ samples.

**Characterization**

XRD patterns of the CH$_3$NH$_3$PbI$_3$ samples were obtained with a Bruker D8 diffractometer (with Cu–Kα radiation). The morphological properties of the material were investigated using a scanning electron microscope (FEI NOVA nano-SEM 600). TEM was performed using a Tecnai F20 FEI TEM equipped with a Gatan 2002 GIF system. The CH$_3$NH$_3$PbI$_3$ solar cells were illuminated using a xenon lamp of 150 W solar simulator (New port model 96000) equipped with an Air Mass 1.5 filter. All electrochemical measurements were performed using a potentiostat (EG&G-PAR 273A). The light intensity incident on the cells was adjusted to 100 mW cm$^{-2}$ using a silicon power meter (Thorlabs S120UV).
Author contributions

VV and MS developed the idea of using graphene/PANI as a conductive protective coating. NR, SK and VV contributed equally to this work. NR, SK and BL devised the experimental plan and performed the experiments. All the authors analyzed and discussed the data and co-wrote the manuscript.

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