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ARTICLE

Robust and Air-Stable Sandwiched Organo-Lead Halide Perovskites for Photodetector Applications

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We report the simplest possible method to date for fabricating robust, air-stable, sandwiched perovskite photodetectors. Unlike conventionally designed photodetectors, our proposed sandwiched structure does not require electron or hole transporting layers or expensive electrodes. We demonstrate that photocurrent and sensitivity are enhanced by an order of magnitude in the MAPbI₃-MAPbBr₃ heterojunction compared to homojunction of their analogues. This simpler approach may have application in the perovskite-only class of solar cells with the goal of scaling up towards commercialization.

Introduction

The discovery of perovskites was a breakthrough in the search for new materials¹⁻³ for future electronic and energy applications, where currently certified photo conversion efficiency (PCE) is reaching 20.1%.^{4,5} Despite the unabated race continues for the PCEs⁶⁻⁹, little work is concentrated on the perovskite photodetectors (PDs).¹⁰ Owing to the direct band gap excitation¹¹, large absorption coefficients¹², small exciton binding energies¹³, low non-radiative Auger recombinations¹⁴ and high ambipolar carrier mobilities¹⁵ perovskites are the promising candidates for the photodetector applications.¹⁶

Being in this regime, however the recent advancements made in perovskite photovoltaic applications that involve various methods of fabrication and complicated architectures, such as the use of a hole-blocking compact TiO₂ layer¹⁷⁻²⁰, perovskite-graphene hybrids²¹, single crystal based²², water-resistant fluororous/ polymer protection²³, the hole transport material p-type 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenylamine)-9,9'-bifluorene (Spiro- MeOTAD)²⁴ and the electron transport layer²⁵

n-type mesoporous titania (mp-TiO₂)²⁶, the PDs built with these components require high vacuum depositions²⁷, additional intermediate layers²⁸, expensive electrodes²⁹ and cumbersome synthetic routes that edge their absorption bandwidth and their overall photosensitivity.

The practical outdoor PD applications of the perovskites are limited due to the degradation and instability of the device

under extended hours of illuminations.³⁰ In addition; various photodetector architectures undergo different degradations due to the fact that the active perovskite is exposed to the moisture, oxygen and temperatures. Homogeneous perovskite thin films deposited by a two-step sequential solution process for successful utilization in the nanostructured scaffolds, suffer from high film surface roughness and adhesion issues.³¹ Most of the PDs are selective at a specific or narrow wavelength regime, due to the limitation of the band gap of the single active perovskite.³² However, the attempts made to grow different encrusted perovskites on top of other to harvest the incident radiation over the broad ranges, were not fruitful because of the challenges posed by the solution processes.³³

The supplementary layer of perovskite deposited on the top, dissolves the perovskite layer beneath it. Therefore, the possibility of benefitting from the graded band gap architectures with two different perovskites remained unsolved to date.

We report a new methodology of fabricating the MAPbI₃ and MAPbBr₃ (MA = CH₃NH₃⁺) perovskite films in a sandwich-like structure for PD applications by the single step process with enhanced controllability, stability and high reproducibility. The simplified architecture we propose negates the use of expensive electrodes, patterning processes, HTL and ETL free (Spiro- MeOTAD and mp-TiO₂ layers respectively), paving the way for their scalable commercialization. The novelty of the current method lies in fabrication strategy, in brief; the MAPbI₃ and MAPbBr₃ films on Glass/FTO are sandwiched and encapsulated. The graded band gaps of two perovskites (MAPbI₃ and MAPbBr₃), allows the broad spectral absorption and, therefore, improved the PDs efficiency. We firmly believe such a novel encapsulated facile fabrication protects the PDs degradation from the oxygen moisture and temperatures thereby allowing for the robust handling over large areas, in the outdoor applications.³⁴ The robustness and stability of the sandwiched PD were tested over 180 days. We also present a

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ARTICLE

Journal Name

profound understanding of the interfacial transport mechanisms of the two perovskites sandwiched between the FTO Schottky electrodes.

Materials and Methods

Experimental Details

Lead iodide (99.999% trace metal basis) was purchased from Sigma-Aldrich. MABr and MAI were purchased from Dyesol Limited (Australia). MAPbI₃ film was deposited by solvent engineering technique.¹ Briefly, 1 M MAPbI₃ in gamma-butyrolactone (GBL) and dimethylsulphoxide (DMSO) (7:3 V/V) was spin coated on the substrate at 1000 and 5000 rpm for 10 and 20 s, respectively. Toluene was dropped during the second spin-coating step. MAPbBr₃ thin film was prepared from MAPbI₃ through the halide exchange by MABr vapor. Briefly, MAPbI₃/substrate was placed on a hot plate under vacuum jar and 1 g MABr was distributed around the film, followed by the vacuum evacuation and keeping on the hot-plate at constant 145 °C for 1 h. Black coloured MAPbI₃ film transformed into an orange film, which is a typical colour for MAPbBr₃.

Device Fabrication

The FTO/MAPbI₃ and FTO/MAPbBr₃ thin films prepared respectively from solvent engineering and halide exchange routes, were stacked perpendicularly facing each other with the glass surface outwards as demonstrated in Fig. 1 (steps i, ii and iii). The as-formed sandwiched geometry of the PD (step iv) is then encapsulated by epoxy in nitrogen and dried under vacuum for few hours. Such a configuration ensures protection from humidity degradation in the ambient. Various configurations of homo (MAPbI₃-MAPbI₃) and hetero (MAPbI₃-MAPbBr₃) junctions were fabricated and tested in the current study.

Experimental characterizations

Thin film X-Ray diffraction was carried out on Bruker D8 Advance. UV-VIS steady-state absorption spectra were recorded on Cary 6000i spectrophotometer with an integrating sphere. The photoelectron spectroscopy in the air (PESA) measurement was performed on the perovskite thin films using Riken Photoelectron Spectrometer (Model AC-2). The UV lamp intensity that was pre-calibrated for the light correction was fixed at 50 nW for measurements. Current-Voltage characteristics and photodetection were carried out under A.M. 1.5 G Newport Solar Simulator equipped with Keithley 2400 source measurement unit.

Results and discussion

The MAPbI₃ perovskite films (See experimental details) go through a colour change with complete transformation to MAPbBr₃ using MABr vapor (Fig. 2a and 2b). X-ray diffraction (XRD) was used to evaluate the crystalline properties and phases of perovskite films before and after transformation.³⁵ The XRD pattern in Fig. 2d illustrates that all peaks can be

assigned to the MAPbI₃ tetragonal crystallographic phase.³⁶ The complete transformation to MAPbBr₃ via the vapor assisted solution process (VASP) is also confirmed by the XRD pattern shown in Fig. 2c. MAPbBr₃ XRD peaks are assigned to the cubic Pm-3m space group.

Fig. 1. Schematic illustration of device fabrication (i) MAPbI₃ thin film formation by solvent engineering route. (ii) MAPbBr₃ film formation by halide exchange route under MABr vapor. (iii) MAPbI₃ and MAPbBr₃ thin films on FTO sandwiched and sealed under nitrogen. (iv) Complete device architecture used in the current study.

The Bragg reflections obtained are consistent with previously reported for MAPbBr₃.³⁷ High-intensity peaks obtained before and after transformation provide clear evidence for the preservation of high crystallinity in the films. Fig. 2c, 2d shows the XRD pattern of MAPbBr₃ and MAPbI₃ films used for formation of MAPbBr₃/MAPbI₃ heterojunction before device fabrication (Day 1) and after the device fabrication (Day 180), respectively. As can be seen in the inset of Fig. 2d, after 180 days of PD fabrication, a small change ($\Delta 2\theta = 0.055^\circ$) in the (220) Bragg reflection was observed, which is ascribed to the diffusion of small Br⁻ ions (Ionic radius: 1.96 Å) into the MAPbI₃ interface by substituting big I⁻ ions (Ionic radius: 2.2 Å).³⁸ Further correlation with heterojunction analysis is discussed in the later sections.

Fig. 2. Illustrations of the complete transformation of (a) MAPbI₃ into (b) MAPbBr₃; XRD patterns of (c) MAPbBr₃ and (d) MAPbI₃. Inset in Fig. 2d showing the $\Delta 2\theta$ of (220) Bragg reflection.

The surface morphologies of these films were imaged by scanning electron microscopy (SEM), as shown in Fig. 3. The films show full coverage and well-defined grain structures before and after transformation. The densely packed sub-micron sized grains were observed from the high-resolution cross-sectional SEM images (Fig. 3e and 3f). The thick films > 1 μm are used in the current study as they allow complete absorption of sunlight particularly in the near infrared region. Moreover, the low-cost large area deposition processes like doctor blade coating, printing and gravure coating employ thicker films to ensure the leakage/ pinhole formations during the commercial manufacturing of the devices.³⁹ In addition, interesting features were seen protruding from the MAPbI₃ film grain surfaces that were completely absent from MAPbBr₃.

This was expected as the MAPbI₃ film formation involved the spin casting from DMSO and GBL with high boiling points of 189 °C and 204 °C, respectively, followed by the anti-solvent (Toluene) crystallization. The nuclei formation and crystal growth process involved in the MAPbI₃ perovskite film, in general, occurs when the solution reaches the supersaturation.⁴⁰ However, due to the higher boiling points of solvents used for spun casting, a gradient in the solvent evaporation, during the spin coating is established, hence the formation of small nuclei is observed, which can be possibly attributed to the Ostwald's ripening process.⁴¹ This event is unlikely to occur in the case of MAPbBr₃ because the film formation is due to the halide exchange. Notably, the protruding on the grains of MAPbI₃ would be advantageous for the carrier transport in the heterostructured PD, which will be discussed in later sections. Steady-state absorption spectra in Fig. 4 (a, b), show sharp band-edge cut off from both MAPbI₃ and MAPbBr₃ thin films.³⁵

Fig. 3 SEM images of (a, b) MAPbI₃ and (c, d) MAPbBr₃ at high and low magnifications, respectively. High-resolution cross-sectional SEM shows the submicron-sized grain in (e) MAPbI₃ and (f) MAPbBr₃ thin films.

From the Tauc plots the direct band gaps were estimated as 1.56 eV and 2.26 eV for MAPbI₃ and MAPbBr₃, respectively,

values that agree with those for polycrystalline perovskite thin films reported elsewhere.⁴² Note that the absorption signature of the MAPbI₃ band, centred at ~750 nm is absent from MAPbBr₃ (Fig. 4 (a, b)), confirming the complete transformation via the halide-exchange VASP. The anticipated change in the work function of perovskite films upon exchange of the halide was estimated by photoelectron spectroscopy in the air (PESA). Valence band levels (Fig. 4c) were obtained at 5.38 eV and 5.52 eV for MAPbI₃ and MAPbBr₃, respectively, which is in good agreement with reported values.⁴³ The prototype device fabrication is displayed in insets of Fig. 5. In this architecture, the two-perovskite films are sandwiched between the patterned transparent FTO electrodes. Current-voltage characteristics (Fig. 5a, 5c and 5e) were evaluated for PDs under dark and A.M 1.5 G one-sun Xenon lamp illuminations for homojunctions - MAPbI₃-MAPbI₃, MAPbBr₃-MAPbBr₃ and for heterojunction - MAPbI₃-MAPbBr₃. Unlike the linear dependence of current on the applied bias as was observed during ohmic contact between TiO₂ and FTO¹⁷, the non-linear behaviour, we observe is indicative of a well-established Schottky contact between FTO and perovskite junctions, which can be attributed to the change in work function with the substitution of the halide as measured by PESA.⁴³ The Schottky barrier imposed at equilibrium is overcome upon illumination of photons ($h\nu \geq E_g$ of semiconductor) by the increase in the free carrier density as a result of which the photogenerated electrons and holes separated quickly and thereby reduce the recombinations.⁴⁴ The lowered barrier height upon photon flux illumination assists in tunnelling of carriers and hence the effective transport leading to the amplification of the photocurrent. The situation reverses, for instance, the recombinations and higher Schottky barrier heights upon turning off the photon illumination, resulting in lower dark current.³² Fig. 5 (b, d and f) illustrate that the photocurrent is amplified in the MAPbI₃-MAPbI₃, MAPbBr₃-MAPbBr₃, MAPbI₃-MAPbBr₃ junctions, suggesting that all-perovskite architectures can be promising candidates for forthcoming PD applications. However, photocurrent enhanced significantly at the MAPbI₃-MAPbBr₃ heterojunction compared to either homojunction of their analogues.

Furthermore, the sensitivity was calculated using $S = I_{ph}/I_d$ ⁴⁵ where $I_{ph} = I_p - I_d$, such that I_p is the current under illumination and I_d is the dark current. More specifically, sensitivity was calculated to be ~0.4, ~0.9 and ~43, for MAPbI₃-MAPbI₃, MAPbBr₃-MAPbBr₃ and MAPbI₃-MAPbBr₃ junctions, respectively. As seen from Fig. 2d inset, the variation of (002) peak indicated that MAPb(I_{1-x}Br_x) formed where $1 \leq x \leq 0.05$, suggesting a very thin interfacial mixed halide formation. Such a slight modification at the interface would not deteriorate the device performance as optical band gap remained unaltered according the recent reports.³⁷ However, the exponential growth characteristics of MAPbI₃-MAPbBr₃ junctions was found to be different due to this thin mixed halide formation. It is to be noted that the dark current reduction is likely to be seen in the Schottky diodes due to a thin interfacial layer.⁴⁶

Journal Name

ARTICLE

Fig. 4 Steady-state absorption spectra of (a) MAPbI₃ and (b) MAPbBr₃. The insets are Tauc plots showing the calculated band gaps of the corresponding perovskite. (c) Photo Electron Spectroscopy in Air (PESA) measurements for work function analysis of MAPbI₃ and MAPbBr₃ thin films (d) Schematic band alignment is showing the tunnelling of carriers upon illumination.

Hence, we attribute the reduction in the dark current in the heterojunction due to this mixed halide thin layer formation, as evidenced from the XRD measurements. In the current situation, the photocurrent (I_{ph}), which is one of the crucial estimates of the PD performance, was found to be enhanced in heterojunction MAPbI₃-MAPbBr₃ (Fig. 5f) than in its homojunction analogues. Additionally, the drastic decrease in the dark current in the heterojunction is the integrated advantage of this configuration over homojunction counterparts. The homojunction (MAPbI₃-MAPbI₃) configuration (Fig. 5b, 5d) showed higher current, however, both in the dark and under one sun illumination. Notably the output PD current depends on the interfacial contact and/or the possibility of better junction formations. In a sequential batch of same homo/heterojunction samples, the current under illumination found to be varied. However, the photocurrent and sensitivity remained within tolerable limits for similar configurations. The higher dark currents and low

sensitivity in homojunction (MAPbI₃-MAPbI₃, MAPbBr₃-MAPbBr₃) clearly indicate the poor junction formation compared to heterojunction.

The reversibility and stability of PD were tested by consecutive *ON* and *OFF* temporal photoresponsive cycles under the one-sun conditions at 2V applied bias. The rise and decay time of PD is an important parameter to realize for practical applications. PDs showed rise times of 109 ms, 112 ms and 109 ms and decay times of 97 ms, 120 ms and 94 ms for MAPbI₃-MAPbI₃, MAPbBr₃-MAPbBr₃ and MAPbI₃-MAPbBr₃ junctions, respectively (Fig. 6). However, the heterojunction PD showed better performance compared to homojunction, in terms of the lower dark current of 2.08 nA, the high sensitivity of 43 and a more reasonable on and off ratio (1.11) than did homojunction junctions. The obtained photoresponse time constants values are in comparison with the conventional perovskite photodetector involving ETL/HTL layers.^{17, 47}

Fig. 5 (a, c, e) Current-voltage characteristics of PDs under dark and A.M 1.5 G lamp illuminations; (b, d, f) ON and OFF photo responsive cycles of MAPbI₃-MAPbI₃, MAPbBr₃-MAPbBr₃ and MAPbI₃-MAPbBr₃ junctions, respectively.

Fig. 6 Time constants (Rise and Decay) obtained from the single ON and OFF photoresponsive cycle for (a, b) MAPbI₃-MAPbI₃; (c, d) MAPbBr₃-MAPbBr₃; (e, f) MAPbI₃-MAPbBr₃ junctions, respectively.

Journal Name

ARTICLE

The robustness and stability of the encapsulated device are tested with time. The reversibility and stability of the heterojunction device were tested for 2, 5 and 10 sec cycles over time (Day 180) as shown in Fig. 7.

A small change in the photocurrent (Fig. 7) was observed with time, suggesting the practical applicability of the current strategy. The transport phenomenon occurring at the junction (both homo and hetero) in the sandwiched PD is analysed by the temperature-responsive current-voltage characteristics (Fig. 8, S1, and S2). The current-voltage characteristics were analysed by the single standard carrier thermionic emission equation (1).⁴⁸

$$I = I_0 \left[\exp\left(\frac{qV}{kT}\right) - 1 \right] \quad (1)$$

where I_0 is the saturation current given by equation (2)

$$I_0 = AA^*T^2 \exp\left[\frac{-q\phi_b}{kT} - 1\right] \quad (2)$$

Where q is the electronic charge, ϕ_b is the barrier height, η is the ideality factor, k is the Boltzmann constant, A is the diode area and A^* is the Richardson constant. The temperature dependence of ideality factors was estimated from the semi-logarithmic plot (Fig. 8) using equation (3). Variation in the ideality factor from unity, in this case, indicates that carrier recombination mechanisms are dominating carrier transport. The Richardson constant, A^* , and the zero-bias barrier height, ϕ_{bo} , were estimated from the Richardson plot using equations (2 and 3).

$$\ln \frac{I_0}{T^2} = \ln(AA^*) - \frac{q\phi_{bo}}{KT} \quad (3)$$

The Richardson constant and the zero-bias barrier height were found to be $7.93 \times 10^{-14} \text{ Acm}^{-2} \text{ K}^{-2}$ and $1.54 \times 10^{-5} \text{ Acm}^{-2} \text{ K}^{-2}$ and 0.08 eV and 0.50 eV for MAPbI₃-MAPbI₃ and MAPbI₃-MAPbBr₃ junctions respectively. Smaller Richardson constant values are an indication of inhomogeneity in the form of patches of low and high barrier heights, more seen in the case of homojunction than heterojunctions⁴⁹. The MAPbI₃-MAPbI₃ homojunction also showed three types of conduction mechanisms: a) Ohmic, b) trap-filled limited and c) Child's law. Trap-filled-limited conduction was not dominant at heterojunctions. As shown in Fig. S1 and S2, transport characteristics can be modelled using the space charge limited conduction (SCLC).⁵⁰ The current followed a linear pattern in

the lower voltage bias, where the density of the thermionic emission of electrons present in the

Fig. 7 Photoresponse of MAPbI₃-MAPbBr₃ heterojunction at various ON and OFF cycles demonstrating the stability and reversibility of the photodetector.

bulk of the perovskite is greater than the injection of electrons from electrodes. The typical SCLC comes into play when the injection of carriers through electrode exceeds the bulk carrier density in the perovskite. At relatively higher applied voltages, there is a sudden increase in the current that is associated with trap-assisted SCLC dominating conduction. At higher voltages, the current decreases further and follows power law dependence that indicates the Child regime.

The ohmic regime, where the linear behaviour of a current as a function of voltage, can be modelled using equation (4)⁵¹

$$J_{Ohm} = qn_o\mu \frac{V}{d} \quad (4)$$

Where V is the applied voltage, q is the electronic charge, n_o is the charge carrier density, d is the thickness of the film and μ is the carrier mobility. The Mott–Gurney law, where the slope is 2, can be described by the equation (5)⁵²

$$J_{Child} = \frac{9}{8} \mu \epsilon \frac{V^2}{d^3} \quad (5)$$

At $m > 2$, the system deviates from the Mott–Gurney law ($J \propto V^m$) and the trap-filled-limited SCLC begins to dominate. Carrier injection through electrodes experiences repulsion from the fully filled traps lying in the bulk of the semiconductor. At the threshold voltage (V_{TFL}) (equation (6)), the injected carriers overcome the repulsive forces and a sudden increase in the current is observed, indicating trap-filled-limited SCLC, modelled mathematically by equation (7)⁵³

Fig. 8 Plots showing the (a, c) Richardson constant and zero-bias barrier height, (b, d) Ideality factor variation with temperature for homo and heterojunctions respectively.

$$V_{TFL} = \frac{qN_t d}{2\varepsilon} \quad (6)$$

$$J_t = N_v \mu e^{1-l} \left[\frac{\varepsilon l}{(l+1)H} \right]^l \left[\frac{2l+1}{l+1} \right]^{l+1} \left[\frac{V^{l+1}}{d^{2l+1}} \right] \quad (7)$$

where H is the total trap concentration, N_v is the valence band effective density of states and $l = E_t/k_b T$, where E_t is the energy related to the trap distribution decay. Therefore, the heterojunction has proven favourable to the homojunction in the fabrication of PDs.

Conclusions

In conclusion, we report the simplest possible method to date for fabricating robust, air-stable sandwiched perovskite photodetectors. Unlike conventionally designed PDs, our proposed sandwiched structure does not require HTL, ETL and expensive electrodes. Moreover, the fabricated VASP MAPbI₃ and MAPbBr₃ perovskite films show comparatively high sensitivity, a low dark current in a simple device architecture. The MAPbI₃-MAPbBr₃ perovskite heterojunction exhibited a significant improvement in the photocurrent in comparison with their homojunction analogues. These simpler architectures may have promising applications in the perovskite-only class of solar cells with the goal of future scaling-up towards commercialization.

Notes and references

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ARTICLE

Journal Name

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TOC graphic

We report the simplest possible method to date for fabricating robust, air-stable, sandwiched perovskite photodetectors. Unlike conventionally designed photodetectors, our proposed sandwiched structure does not require electron or hole transporting layers or expensive electrodes. We demonstrate that photocurrent and sensitivity are enhanced by an order of magnitude in the MAPbI₃-MAPbBr₃ heterojunction compared to homojunctions of their analogues.