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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 fluorous/ 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 illuminations30 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
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). MAPbI$_3$ film was deposited by solvent engineering technique. Briefly, 1 M MAPbI$_3$ 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. MAPbBr$_3$ thin film was prepared from MAPbI$_3$ through the halide exchange by MABr vapor. Briefly, MAPbI$_3$/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 MAPbI$_3$ film transformed into an orange film, which is a typical colour for MAPbBr$_3$.

Device Fabrication

The FTO/MAPbI$_3$ and FTO/MAPbBr$_3$ 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 (MAPbI$_3$/MAPbI$_3$) and hetero (MAPbI$_3$/MAPbBr$_3$) 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 MAPbI$_3$ perovskite films (See experimental details) go through a colour change with complete transformation to MAPbBr$_3$ 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. The XRD pattern in Fig. 2d illustrates that all peaks can be assigned to the MAPbI$_3$ tetragonal crystallographic phase. The complete transformation to MAPbBr$_3$ via the vapor assisted solution process (VASP) is also confirmed by the XRD pattern shown in Fig. 2c. MAPbBr$_3$ XRD peaks are assigned to the cubic Pm-3m space group.
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 submicron sized grains were observed from the high-resolution cross-sectional SEM images (Fig. 3e and 3f). The thick films before and after transformation. The densely packed submicron-sized grain in

Fig. 3 SEM images of (a, b) MAPbI$_3$ and (c, d) MAPbBr$_3$ at high and low magnifications, respectively. High-resolution cross-sectional SEM shows the submicron-sized grain in (e) MAPbI$_3$ and (f) MAPbBr$_3$ thin films.

From the Tauc plots the direct band gaps were estimated as 1.56 eV and 2.26 eV for MAPbI$_3$ and MAPbBr$_3$, respectively, values that agree with those for polycrystalline perovskite thin films reported elsewhere. Note that the absorption signature of the MAPbI$_3$ band, centred at ~750 nm is absent from MAPbBr$_3$ (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 MAPbI$_3$ and MAPbBr$_3$ respectively, which is in good agreement with reported values. 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 homojunction - MAPbI$_3$-MAPbI$_3$-MAPbBr$_3$ and for heterojunction - MAPbI$_3$-MAPbBr$_3$. Unlike the linear dependence of current on the applied bias as was observed during ohmic contact between TiO$_2$ and FTO$^{40}$, 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. The Schottky barrier imposed at equilibrium is overcome upon illumination of photons (h$\nu$Eg 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. 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. Fig. 5 (b, d and f) illustrate that the photocurrent is amplified in the MAPbI$_3$-MAPbI$_3$-MAPbI$_3$, MAPbBr$_3$-MAPbBr$_3$, MAPbI$_3$-MAPbBr$_3$, junctions, suggesting that all-perovskite architectures can be promising candidates for forthcoming PD applications. However, photocurrent enhanced significantly at the MAPbI$_3$-MAPbBr$_3$ heterojunction compared to either homojunction of their analogues. Furthermore, the sensitivity was calculated using $S = I_d/I_u$ where $I_d = I_{d0} - I_d$ such that $I_u$ 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 MAPbI$_3$-MAPbI$_3$, MAPbBr$_3$-MAPbBr$_3$ and MAPbI$_3$-MAPbBr$_3$ junctions, respectively. As seen from Fig. 2d inset, the variation of (002) peak indicated that MAPb(I$_x$Br$_{1-x}$) formed where 1≤x≤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. However, the exponential growth characteristics of MAPbI$_3$-MAPbBr$_3$ 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.
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 MAPbI$_3$-MAPbBr$_3$ (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 (MAPbI$_3$-MAPbI$_3$) 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 (MAPbI$_3$-MAPbI$_3$, MAPbBr$_3$-MAPbBr$_3$) 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 MAPbI$_3$-MAPbI$_3$, MAPbBr$_3$-MAPbBr$_3$ and MAPbI$_3$-MAPbBr$_3$ 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 Pcs under dark and A.M 1.5 G lamp illuminations; (b, d, f) ON and OFF photo responsive cycles of MAPbI$_3$-MAPbI$_3$, MAPbBr$_3$-MAPbBr$_3$ and MAPbI$_3$-MAPbBr$_3$ junctions, respectively.

Fig. 6 Time constants (Rise and Decay) obtained from the single ON and OFF photoresponsive cycle for (a, b) MAPbI$_3$-MAPbI$_3$; (c, d) MAPbBr$_3$-MAPbBr$_3$; (e, f) MAPbI$_3$-MAPbBr$_3$ junctions, respectively.
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).\(^{(2)}\)

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

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

\[
I_0 = A* T^2 \exp \left[ -\frac{q\phi_b}{kT} - 1 \right]
\]

Where \(q\) is the electronic charge, \(\phi_b\) is the barrier height, \(\eta\) 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, \(\phi_{bo}\), were estimated from the Richardson plot using equations (2 and 3).

\[
\ln \frac{I}{T^2} = \ln(A*\eta) - \frac{q\phi_{bo}}{kT}
\]

The Richardson constant and the zero-bias barrier height were found to be 7.93 \(\times 10^{14}\) Acm\(^{-2}\) K\(^{-2}\) and 1.54 \(\times 10^{5}\) Acm\(^{-2}\) K\(^{-1}\) and 0.08 eV and 0.50 eV for MAPbI\(_3\)-MAPbI\(_3\) and MAPbI\(_3\)-MAPbBr\(_3\) 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 heterojunctions\(^{(3)}\). The MAPbI\(_3\)-MAPbI\(_3\) 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)\(^{(4)}\). The current followed a linear pattern in the lower voltage bias, where the density of the thermionic emission of electrons present in the 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)\(^{(5)}\)

\[
J_{\text{Ohm}} = qn_o \mu \frac{V}{d}
\]

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 \(\mu\) is the carrier mobility. The Mott–Gurney law, where the slope is 2, can be described by the equation (5)\(^{(6)}\)

\[
J_{\text{Child}} = \frac{9}{8} \mu \varepsilon \varepsilon_0 \varepsilon_0 V^2
\]

At \(m > 2\), the system deviates from the Mott–Gurney law (\(J \propto V^2\)) 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 \((V_{\text{TH}})\) (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)\(^{(7)}\)
expensive electrodes. Moreover, the fabricated VASP MAPbI
proposed sandwiched structure does not require HTL, ETL and
photodetectors. Unlike conventionally designed PDs, our
work reported here. B.M. and M.I.S. contributed equally to this

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Notes and references
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TOC graphic

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