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New Concepts

Development of flexible, transparent optoelectronic devices has received enormous interest owing to their potential applications in smart windows and wearable electronics. Mechanical flexibility of the photodetectors can further inflate the possible range of applications towards wearable electronics and adaptability to curved surfaces. Traditional photodetectors are rigid, brittle, completely opaque and confined to small areas with limited spectral response. Hence, the development of large-area transparent photodetectors with excellent mechanical flexibility and high photoresponse over a broad spectral range can meet the increasing demands of high-performance optoelectronic devices. Here, we fabricate guanidinium incorporated metal halide perovskite ($\text{MA}_{1-x}\text{Gua}_x\text{PbI}_3$, $x=0$ to 0.65) random percolative microstructures (RPMs) using a single step ultra-fast spray coating technique, which shows transparency of $\sim 50\%$, greatly enriched the photoresponse and stability. Furthermore, the RPMs based photodetectors displayed excellent mechanical flexibility under wide range of bending angles and large number of binding cycles. Combining all these features including high performance, stability, transparency and flexibility in a photodetector is unmatched and the performance is second to none.

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Large-area Transparent Flexible Guanidinium Incorporated MAPbI₃ Microstructures for High-performance Photodetectors with Enhanced StabilityReceived 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Unveiling the transparency and flexibility in perovskite-based photodetectors with superior photoresponse and environmental stability remains an open challenge. Here we report on the guanidinium incorporated metal halide perovskite (MA_{1-x}Gua_xPbI₃, x=0 to 0.65) random percolative microstructures (RPMs) fabrication by a single step using ultra-fast spray coating technique. Remarkably, RPMs over a large area of 5 × 5 cm² on flexible substrates with a transparency of ~ 50% can be achieved with enriched environmental stability. Transparent photodetectors based on MA_{1-x}Gua_xPbI₃ (x=0.12) RPMs manifest excellent performance with responsivity 187 A/W, detectivity 2.23×10¹² jones and external quantum efficiency of 44115%. Additionally, the photodetectors exhibited superior mechanical flexibility under wide range of bending angles and large number of binding cycles. Integrating features including transparency, high performance, stability, flexibility and scalability within a photodetector is unmatched and holds potential for novel applications in transparent and wearable optoelectronic devices.

Transparent photodetectors have attracted tremendous research attention in recent years owing to the potential applications in next generation optoelectronic devices.¹⁻³ Mechanical flexibility of the photodetectors can further inflate the possible range of applications towards wearable electronics and adaptability to curved surfaces.⁴⁻⁸ Traditional photodetectors are rigid, brittle, completely opaque and confined to small areas with limited spectral response.^{9-11,12} Hence, the development of large-area transparent photodetectors with excellent mechanical flexibility and high photoresponse over a broad spectral range is essential to meet the increasing demands of high performance optoelectronic

devices.⁵ However, combining high photoresponsivity, mechanical flexibility and transparency features all together in a single device along with large-area scalability remains an uphill task.

Recently, organic-inorganic hybrid perovskites have emerged as excellent candidates for high performance optoelectronic devices.^{13-18,19} A variety of compositions for the cations (MA, FA, BA) and halides (Cl, Br, I) have been used to design superior organic-inorganic hybrid perovskites.²⁰⁻²³ The pure phase of organic-inorganic perovskites are synthesized using mechanochemistry and solution processed methods.²⁴ However, a continuous perovskite thin film is opaque in the visible region, which is not compatible for transparent electronics. However, transparent photodetectors have been realized through patterning perovskite without compromising the optoelectronic properties. Song *et al.* have shown the fabrication of perovskite network-based photodetectors with limited transparency and photoresponse.³ In addition to the patterning of perovskites and improvement in the device efficiencies, ambient stability issue remains a great challenge. The decomposition of perovskites due to sensitivity towards oxygen and moisture²⁵ and intrinsic halide segregation^{26,27} create a major hurdle for the stability. To overcome the stability issue, alternate all-inorganic perovskites negating volatile organic cations have been proposed with promising optoelectronic properties.^{28-30,31,32} However, organic alternatives with an appropriate ionic radius to accommodate within the inorganic Pb-I framework is limited primarily because of the mismatch in the size to maintain an adequate Goldschmidt tolerance factor.^{33,34} Recently, organic cation Guanidinium (C(NH₂)₃⁺, Gua) has been incorporated into the pre-existing 3D perovskite lattice of MAPbI₃.³⁵ Gua containing a larger ionic radius than MA, results in higher limit of Goldschmidt tolerance factor, can insert into the crystal unit of MAPbI₃ to form mixed cation perovskite MA_{1-x}Gua_xPbI₃ (0 < x < 0.25).^{33,35} An enhanced thermal and environmental stability along with longer charge carrier lifetime compared to pure MAPbI₃ have been obtained upon Gua incorporation in a lower

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Fig. 1 (a) Schematic illustration of spray coating process. SEM images of RPMs fabricated using (b, c, f) $MAPbI_3$ and (d, e, g) $MA_{0.88}Gua_{0.12}PbI_3$. (h) Photograph of $MA_{0.88}Gua_{0.12}PbI_3$ RPMs on PET substrate over a large area of 5x5 cm². (i, j) XRD patterns of $MA_{1-x}Gua_xPbI_3$ ($x = 0, 0.12, 0.33$ and 0.65) RPMs. (k) Comparison of UV-vis spectra and (l) Transmittance spectra of $MAPbI_3$ and $MA_{0.88}Gua_{0.12}PbI_3$ RPMs.

limit. These findings were beneficial to achieve $MA_{1-x}Gua_xPbI_3$ based solar cells with enhanced performance.³⁵⁻³⁸ However, there is no attempt to fabricate transparent perovskite photodetectors with mixed cations to our knowledge till this date.

Here we developed a simple, solution processed and scalable single-step spray coating route for the formation of random percolative microstructures (RPMs) of $MA_{1-x}Gua_xPbI_3$ perovskites with $\sim 50\%$ transparency. Fabrication of transparent photodetectors using the RPMs leads to record high Figure-of-merits (FOMs) exhibiting photosensitivity of $\sim 41500\%$, responsivity of ~ 187 A/W, detectivity of $\sim 2.23 \times 10^{12}$ Jones and EQE of $\sim 44115\%$. These FOMs are superior in comparison to the reported opaque mixed cationic perovskite-based photodetectors and commercially available silicon-based photodetectors. We have thoroughly investigated the stability of RPMs of $MA_{1-x}Gua_xPbI_3$ by aging the devices in ambient conditions (humidity levels $\sim 45-55\%$) over 30 days. A large enhancement in the stability of photodetectors fabricated with RPMs of $MA_{1-x}Gua_xPbI_3$ is observed in comparison to the $MAPbI_3$ -based photodetectors. Furthermore, we demonstrated the mechanical flexibility of the photodetectors under wide range of bending angles and number of bending cycles.

Guanidinium cation incorporated $MAPbI_3$ precursor solutions are prepared by dissolving GuaI, MAI and PbI_2 at different molar ratio in anhydrous N, N-dimethylformamide (DMF) (Experimental Methods for details, ESI[†]). The precursor solutions are spray coated on glass or PET substrates as shown in the Fig. 1a. Optimal trade-off between the transparency and interconnectivity of perovskite microstructures is achieved by controlling various spray coating parameters (Experimental Methods, ESI[†]). In brief, spray coating is performed for 4 seconds on pre-heated ($110^{\circ}C$) substrate, which instantaneously formed RPMs of perovskite. Optical microscope images reveal perforated microstructures of perovskite over a large substrate area (Fig. S1, ESI[†]). Apparently macroscopic images of the RPMs formed through spray coating process are independent of the Gua cation composition (Fig. S2, ESI[†]). An excellent interconnectivity of the RPMs is obtained for both the $MAPbI_3$ and $MA_{1-x}Gua_xPbI_3$ (Fig. 1b-e, Fig. S3, ESI[†]). However, higher resolution scanning electron microscopic (SEM) images reveal different grain morphologies of the RPMs of $MAPbI_3$ and $MA_{1-x}Gua_xPbI_3$ with variation of packing (Fig. 1f and g). Pristine $MAPbI_3$ RPMs shows corrugations (Fig. 1f) whereas $MA_{0.88}Gua_{0.12}PbI_3$ RPMs shows a smooth surface morphology and improved interconnectivity (Fig. 1g).

Fig. 2 Photoresponse characteristics of MA_{0.88}Gua_{0.12}PbI₃ RPMs based photodetectors. (a) Schematic of the photodetector measurement setup and device structure. (b, c) SEM images of the pre-patterned Au electrodes on top of SiO₂/Si substrate. (d) Current-voltage (I-V) curves of the photodetector under the illumination of white light with intensity of 100 mW/cm² (AM1.5G) and in dark (semi-logarithmic scale). (e) I-V curves of photodetector illuminated with different light intensities 8.2, 4.7, 3, 0.8 and 0.1 mW/cm² respectively. (f) Photocurrent as a function of incident light intensity at constant bias of 0.9 V. (g) photocurrent of photodetector under different incident wavelengths at constant bias of 0.9 V. (h) Responsivity, detectivity and (i) External quantum efficiency of the photodetector as a function of wavelength under an applied bias of 0.9 V.

Interconnected platelets with voids are observed upon increasing the Gua content in the mixed cation perovskites (Fig. S3c, ESI[†]). Fig. 1h shows a photograph of the MA_{0.88}Gua_{0.12}PbI₃ RPMs on a PET sheet with large area of 5 × 5 cm², which clearly manifests the uniformity and transparency. Therefore, the spray coating process implemented here is not only an ultra-rapid process but also scalable to large area.

We carried out X-ray diffraction (XRD) measurements on pristine MAPbI₃ and MA_{1-x}Gua_xPbI₃ RPMs. XRD reveals tetragonal phase of the MAPbI₃ with (110), (220), (310), (224), and (314) reflections at 2θ of 14.2, 28.6, 31.9, 40.6 and 43.24, respectively (Fig. 1i). The tetragonal phase of MAPbI₃ retains after incorporation of Gua cations still a lower extent (0 < x ≤

0.25) by direct substitution of MA, forming a mixed MA_{1-x}Gua_xPbI₃ phase.^{35,38} A closer inspection of (110) and (220) reflections disclose a gradual shift towards lower angles upon incorporation of Gua in MAPbI₃, as reported previously (Fig. 1j).^{35,38} The observed shift of diffraction peaks is attributed to expansion of the unit-cell volume due to the substitution of MA with larger sized Gua cation in MAPbI₃ crystal structure.³⁸ Notably, for x=0.33 Gua content additional XRD peaks appears at 2θ values of 6.72 and 9.33 belongs to pure GuaPbI₃ and further increase of higher Gua content (x= 0.65), the reflection peak at 9.33 is shifted to 8.71 (see red square boxes in Figure 1i, Fig. S4, ESI[†]). Incorporation of Gua in MAPbI₃ causes local distortion in the crystal lattice due to the mismatch in size with

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respect to the MA cation which is manifested by a broadening and shifting of the peaks with different Gua content. Earlier reports demonstrated formation of phase-separated GuaPbI_3 upon incorporation of higher content of Gua cations.^{35,38} Our XRD and SEM observations also suggest formation of phase-separated GuaPbI_3 with larger Gua content, which is corroborated with the reported literatures.³⁸

Since larger content of Gua gradually leads to the GuaPbI_3 phase, we have designed photodetectors with a low content of Gua ($\text{MA}_{0.88}\text{Gua}_{0.12}\text{PbI}_3$) and compared with the pristine MAPbI_3 . Comparison of UV-vis absorption spectra (Fig. 1k) and transparency (Fig. 1l) of MAPbI_3 and $\text{MA}_{0.88}\text{Gua}_{0.12}\text{PbI}_3$ RPMs clearly demonstrate insignificant change in the shape of the spectra. However, a slight decrease of the absorption edge position of $\text{MA}_{0.88}\text{Gua}_{0.12}\text{PbI}_3$ suggests an increase in the bandgap, which is attributed to the local distortions at the Gua neighboring positions owing to the formation of new bonds and expansion of crystal unit.^{35,38} The similarity in the absorption spectra reveals that the substitution of MA by Gua effectively stabilizes the 3D perovskite phase of MAPbI_3 . Average visible transmittance (AVT) is defined as the mean transmittance between 370 nm and 740 nm visible region.^{39,40} We have estimated the AVT values for pristine MAPbI_3 and $\text{MA}_{0.88}\text{Gua}_{0.12}\text{PbI}_3$ RPMs prepared on glass substrate to be ~ 50%, which is consistent with the calculated average fill factor of ~ 56% measured from optical microscope images (Fig. S5, ESI†). The UV-vis absorption spectrum and transparency with higher content of Gua also showed similar spectra (Fig. S6, ESI†). Therefore, the fabricated perovskite RPMs are transparent and are independent of mixed cation composition.

We have measured the photoresponse of $\text{MA}_{0.88}\text{Gua}_{0.12}\text{PbI}_3$ RPMs under the illumination of light and in the dark. The schematic representation of the photodetector device structure and measurement setup is shown in Fig. 2a. The SEM image shows a spacing of 100 nm of the Au electrodes deposited on top of SiO_2/Si substrate (Fig. 2b and 2c). Photosensitivity (on/off ratio) defined by $(I_{\text{light}} - I_{\text{dark}})/I_{\text{dark}}$, is estimated to be ~ 41500% at a low operating bias voltage of ~ 0.9 V (Fig. 2d). The photocurrent of $\text{MA}_{0.88}\text{Gua}_{0.12}\text{PbI}_3$ RPMs is increased by three orders of magnitude under the illumination of light (Fig. 2d). The measured photosensitivity is higher compared to reported opaque mixed cation perovskite-based photodetectors (Table S1).^{41–43} Furthermore, we studied the photoresponse behavior of the $\text{MA}_{0.88}\text{Gua}_{0.12}\text{PbI}_3$ devices with various light intensities ranging from ~ 100 $\mu\text{W}/\text{cm}^2$ to ~ 8.2 mW/cm^2 (Fig. 2e). The photoresponse indicates a linear dependency of light intensity (Fig. 2f), which is essential for reliable photodetector applications. The plot is fitted with the power law expression $I = \alpha P^\beta$ where α is a constant for a specific wavelength, P is the

illuminated light intensity, and the exponent β is the response of the photocurrent to the incident light intensity. The best fitting curve gives a linear behavior with exponent value $\beta = 0.58$ (standard error 0.0236). This fractional power dependence ($0.5 < \beta < 1.0$) indicates existence of electron-hole recombination and trapping of charge carriers.^(44, 45) The photoresponse of the $\text{MA}_{0.88}\text{Gua}_{0.12}\text{PbI}_3$ RPMs measured under the illumination of monochromatic lights at various wavelengths exhibits photosensitivity in entire visible region (Fig. 2g). The performance of the photodetector is further characterized by measuring the FOMs such as responsivity (R), detectivity (D), and external quantum efficiency (EQE) (Fig. S7, ESI†) at a low operating voltage of 0.9 V. The responsivity of the photodetector determines the generated photocurrent for a defined intensity of light. $\text{MA}_{0.88}\text{Gua}_{0.12}\text{PbI}_3$ RPMs based photodetectors demonstrate a robust spectral responsivity in the entire visible region with a maximum responsivity of 187 A/W at a wavelength 700 nm (Fig. 2h). A maximum detectivity of 2.23×10^{12} jones at wavelength 700 nm is obtained from the $\text{MA}_{0.88}\text{Gua}_{0.12}\text{PbI}_3$ photodetector (Fig. 2h). We measured the EQE of transparent mixed cation $\text{MA}_{0.88}\text{Gua}_{0.12}\text{PbI}_3$ RPMs photodetectors to be 44115% (Fig. 2i), which is the best among the transparent photodetectors and relatively higher in comparison to the other photodetectors (Table S1, S2, ESI†).^{41–43} On the other hand, the responsivity of pristine MAPbI_3 and $\text{MA}_{0.67}\text{Gua}_{0.33}\text{PbI}_3$ RPMs based photodetectors are 48 A/W and 135 A/W respectively (Table 1, and Fig. S7, ESI†). Moreover, MAPbI_3 and $\text{MA}_{0.67}\text{Gua}_{0.33}\text{PbI}_3$ RPMs display a lower detectivity of 6.78×10^{11} Jones and 1.61×10^{12} Jones and EQE of 12396% and 30737%, respectively compared to the $\text{MA}_{0.88}\text{Gua}_{0.12}\text{PbI}_3$ RPMs photodetectors (Table 1, and Fig. S7, ESI†). Hence, the RPMs photodetectors fabricated with $\text{MA}_{0.88}\text{Gua}_{0.12}\text{PbI}_3$ showed significantly improved photoresponse compared to MAPbI_3 and adequate improvement compared to $\text{MA}_{0.67}\text{Gua}_{0.33}\text{PbI}_3$ devices. To the best of our knowledge, the performance of the $\text{MA}_{0.88}\text{Gua}_{0.12}\text{PbI}_3$ based transparent photodetectors reported here is the highest among the mixed cation perovskite-based photodetectors and transparent perovskite photodetectors (Table S1 and S2, ESI†).^{46–49}

Table 1. Comparison of performances of MAPbI_3 , $\text{MA}_{0.88}\text{Gua}_{0.12}\text{PbI}_3$ and $\text{MA}_{0.67}\text{Gua}_{0.33}\text{PbI}_3$ based RPMs photodetectors.

Parameter at 0.9 V	MAPbI_3	$\text{MA}_{0.88}\text{Gua}_{0.12}\text{PbI}_3$	$\text{MA}_{0.67}\text{Gua}_{0.33}\text{PbI}_3$
Responsivity (A/W)	48	187	135
Detectivity (Jones)	6.78×10^{11}	2.23×10^{12}	1.61×10^{12}
EQE (%)	12396	44115	30737

Fig. 3 Transient photoresponse of MA_{0.88}Gua_{0.12}PbI₃ RPMs based photodetectors. (a) Schematic illustration of the transient photoresponse measurement setup coupled with modulated optical chopper, oscilloscope, and red laser diode ~ 650 nm at an applied bias of 3 V. (b) Transient photocurrent at different frequencies 20 Hz, 40 Hz, 60 Hz, 80 Hz and 100 Hz. (c) Rise time and fall times are estimated at 100 Hz where black curve represents experimental data, red and cyan curves are the exponential fits, respectively. (d) Normalized photoresponse as a function of modulated light frequency. The cut-off frequency (f_{3dB}) is 495 Hz, which is marked with black dotted line.

The robust photodetector performance can be explained due to the formation of mixed-cation phase in MA_{0.88}Gua_{0.12}PbI₃ where MA interacts with the Gua cations. Recent studies suggested incorporation of Gua into 3D perovskite lattices despite of size mismatch between Gua and MA forming a mixed phase.^{35,38} However, incorporation of Gua occurs till a low limited concentration because of the saturation of the 3D PbI₆ octahedral to accommodate larger Gua cations. Hence, a phase separation takes place in the form of GuaPbI₃ when larger content of Gua is used.^{35,38} Gua cations undergo rapid reorientation on the picosecond time scale, an order of magnitude faster than MA, imparting charge carrier stabilization through the electron–rotor interaction which leads to a long charge carrier lifetime.^{34,50} Density functional theory calculations revealed an enhanced stability of the mixed cation perovskite upon Gua incorporation exhibiting a highly negative formation enthalpy.³⁸ Additionally, introduction of Gua increases the number of hydrogen bonds in comparison to MA

imposing the structural stability. Incorporation of Gua imparts strain on the crystal lattice due to bulky nature of Gua cations. Hence, a change in the lattice structure occurs to accommodate Gua cations, which is reflected in the XRD measurements (Fig. 1i and j) showing a small shift with respect to the main reflection of pure MAPbI₃. In addition to the stabilization effect provided by rapid Gua reorientation, the additional strain may adversely affect charge carrier stability. The improved stability, long charge carrier lifetime, diminishing the recombination rate and trap state density upon Gua incorporation have significant implications for the observed robust performance of the MA_{0.88}Gua_{0.12}PbI₃ photodetector.^{36,38,51–54} This observation is in-line with the improved performance of mixed cation solar cells upon Gua incorporation.^{36,38,51–54}

Fig. 3a illustrates the schematic representation of response time measurement setup along with a laser (650 nm, 3 mW) and optical chopper. We have measured the transient photoresponse of MA_{0.88}Gua_{0.12}PbI₃ RPMs based devices using

Fig. 4 (a) Photographs of $\text{MA}_{0.88}\text{Gua}_{0.12}\text{PbI}_3$ RPMs on flexible PET substrates at various bending angles of 20°, 30°, 45°, and 60° respectively. (b) Plot of photocurrent and dark current with respect to time under different bending angles. (c) Photo switching measurements under the illumination of red light (650 nm) and in dark with the device various bending angles 0° (flat), 20°, 30°, 45°, and 60° respectively. (d) Photocurrent and dark currents as a function of bending cycles up to 1000 times at a bending angle of 60°. The inset shows photographs of the device in flat and bent configurations. Stability test: (e) Photoresponse of the $\text{MA}_{0.88}\text{Gua}_{0.12}\text{PbI}_3$ RPMs measured over 30 days. (f) Normalized photoresponse of MAPbI_3 and $\text{MA}_{0.88}\text{Gua}_{0.12}\text{PbI}_3$ photodetectors with aging for different days.

optical chopper with frequencies ranging from 20 Hz to 1000 Hz at 3 V applied bias. Fig. 3b shows the photoresponse of $\text{MA}_{0.88}\text{Gua}_{0.12}\text{PbI}_3$ RPMs under modulated chopper frequencies of 20 Hz, 40 Hz, 60 Hz, 80 Hz, and 100 Hz respectively. The photoresponse clearly manifests a sharp rise/fall and saturation of the photocurrent when the device is exposed periodically to light (light ON) and dark (light OFF) states. The photoswitching is successfully performed for 800 ON/OFF cycles at 100 Hz frequency (Fig. S8, ESI†). Fig. 3c represents a single ON/OFF

cycle, where the rise time (t_r) and fall time (t_f) are estimated by fitting the photoresponse curve with exponential functions (ESI†).⁵⁵ The rise and fall time of the $\text{MA}_{0.88}\text{Gua}_{0.12}\text{PbI}_3$ photodetector is measured to be $t_r \sim 390 \mu\text{s}$ and $t_f \sim 460 \mu\text{s}$ respectively. Furthermore, we measured normalized photoresponse as a function of frequency ranging from 20 to 1000 Hz (Fig. 3d). The cut-off frequency ($f_{-3\text{dB}}$), the frequency at which photoresponse becomes half of its initial value, is estimated to be ~ 495 Hz. Such a higher value of $f_{-3\text{dB}}$ is beneficial

in increasing the data extraction speed and to enhance the capture capacity of transient signals.

The mandate of next generation photodetectors is to sense the light with excellent mechanical flexibility and environment stability. In order to realize photoresponse in flexible conditions, we spray coated $\text{MA}_{0.88}\text{Gua}_{0.12}\text{PbI}_3$ RPMs on flexible PET substrates with pre-fabricated Ag electrodes (Fig. S9, ESI†). The photodetector fabricated on PET is shaped into curved surfaces with various bending angles of 20°, 30°, 45° and 60° for photodetection (Fig. 4a). The photocurrent measurements are carried out in flat and bending conditions under the continuous illumination of 650 nm laser light (3 mW) at an applied bias voltage of 3V for testing the mechanical flexibility of the devices. The photocurrent and dark current in flat and various bending conditions displayed a minimal change (Fig. 4b). This behavior is attributed to the strain tolerance of the perovskite RPMs under deformation. Furthermore, we evaluated the photoswitching reversibility at different bending angles, where current is recorded under ON/OFF cycles of light at 3 V (Fig. 4c). The device demonstrates excellent photoswitching reversibility over multiple ON/OFF cycles irrespective of the bending angles. The reliability and robustness of the devices is tested by performing light ON/OFF cycles at 60° bending angle for 1000 cycles. The corresponding dark/photocurrents are recorded on regular intervals and plotted as function of number of bending cycles (Fig. 4d). The photoresponse is persistent and nearly unchanged in both the flat and bent conditions, which proves robustness and mechanical flexibility of $\text{MA}_{0.88}\text{Gua}_{0.12}\text{PbI}_3$ RPMs based photodetectors. The performance characteristics of the photodetectors fabricated with larger electrode gap of 100 μm on PET substrates measured and calculated. A maximum responsivity of $\sim 275 \text{ mA/W}$, detectivity of $\sim 2.43 \times 10^{11} \text{ jones}$ and EQE of $\sim 68.2\%$ were obtained. These values are lower compared to the devices fabricated with electrode gaps of 100 nm. Such a decrease of the photodetector performance parameters is expected owing to the longer channel length of the device.^{56,57} Further, we have tested the environmental stabilities of $\text{MA}_{0.88}\text{Gua}_{0.12}\text{PbI}_3$ and MAPbI_3 RPMs based photodetectors over a period of 30 days in ambient conditions. The photocurrent is measured under the illumination of white light source ($\sim 8.2 \text{ mW/cm}^2$) at a bias voltage of 0.9 V. The devices fabricated with $\text{MA}_{0.88}\text{Gua}_{0.12}\text{PbI}_3$ showed a considerable stable response over 30 days under the dark and light illumination (Fig. 4e). In comparison, MAPbI_3 based photodetectors tested in the similar conditions show a significantly decreased photoresponse after 10 days and the photoresponse completely degraded in 20 days (Fig. 4f and Fig. S10, ESI†). These measurements demonstrate the stability and mechanical flexibility along with excellent photodetection capabilities of the transparent $\text{MA}_{0.88}\text{Gua}_{0.12}\text{PbI}_3$ RPMs based perovskite photodetectors.

In summary, transparent and flexible photodetectors based on perovskite $\text{MA}_{1-x}\text{Gua}_x\text{PbI}_3$ RPMs are fabricated for the first time. The RPMs fabricated over a large area $5 \times 5 \text{ cm}^2$ using an ultra-fast spray coating method resulted in $\sim 50\%$ transparency. Photodetectors fabricated with $\text{MA}_{0.88}\text{Gua}_{0.12}\text{PbI}_3$ RPMs showed

excellent FOMs with photosensitivity $\sim 41500\%$, responsivity $\sim 187 \text{ A/W}$, detectivity $\sim 2.23 \times 10^{12} \text{ Jones}$, EQE $\sim 44.15\%$ and response time of 390 μs . To the best of our knowledge, these FOMs are the best among the reported photodetectors fabricated with mixed cation perovskites. The RPMs photodetectors displayed matching photoresponse for ~ 1000 bending cycles over wide range of bending angles demonstrating the robust mechanical flexibility. Furthermore, the Gua incorporated perovskites displayed prominently enhanced environment stability in comparison to the pristine MAPbI_3 . Unmatched performance, enhanced stability and mechanical flexibility combined with transparency of the $\text{MA}_{1-x}\text{Gua}_x\text{PbI}_3$ photodetectors could open up new applications in transparent windows, security gadgets and wearable electronics. The preparation of transparent RPMs demonstrated here may be extended towards the fabrication of transparent smart windows for solar energy harvesting.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by SERB projects “EMR/2014/000664 & ECR/2017/003264”. We acknowledge the Technical Research Centre of IACS. G.S.K. and P.K.S. acknowledges the DST INSPIRE Programme for fellowship. M.H. acknowledges the UGC for fellowship.

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