Carrier photodynamics in 2D perovskites with solution-processed silver and graphene contacts for bendable optoelectronics

Ridwan F. Hossain1,2, Misook Min1, Liang-Chieh Ma1, Shambhavi R. Sakri1 and Anupama B. Kaul1,2✉

Silver (Ag) and graphene (Gr) inks have been engineered to serve as efficient electrical contacts for solution-processed two-dimensional (2D) organo-halide $(\text{CH}_3(\text{CH}_2)_3\text{NH}_3)\text{(CH}_3\text{NH}_3)$$_n$$\cdot$$\text{Pb}_x\text{I}_{3n+1}$ ($n = 4$) layered perovskites, where all inkjet-printed heterostructure photodetectors (PDs) were fabricated on polyimide (PI) substrates. To date, limited studies exist that compare multiple contacts to enable high-performance engineered contacts to 2D perovskites. Moreover, of these few reports, such studies have examined contacts deposited using vapor-based techniques that are time-consuming and require expensive, specialized deposition equipment. In this work, we report on the inkjet printed, direct contact study of solution-processed, 2D perovskite-based PDs formed on flexible PI substrates. Solution processing offers a cost-effective, expedient route for inkjet printing Gr and Ag using a dispersion chemistry developed in this work that is compatible with the underlying 2D perovskite layer to construct the PDs. The wavelength $\lambda$-dependent photocurrent $I_p$ peaked at $\lambda = 630$ nm for both PDs, consistent with the bandgap $E_g \approx 1.96$ eV for our semiconducting 2D perovskite absorber layer. The external quantum efficiency was determined to be 103% for Ag-perovskite PDs, where strain-dependent bending tests were also conducted to reveal the opto-mechanical modulation of the photocurrent in our devices.

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INTRODUCTION

Organic–inorganic hybrid perovskites described by the formula $A\text{BX}_3$, $A = \text{CH}_3\text{NH}_3$; $B = \text{Pb}^{2+}$ or $\text{Sn}^{2+}$; and $X = \text{Cl}^–$, $\Gamma^–$, $\text{Br}^–$, have recently emerged as attractive materials for solar energy conversion$^1$–$^3$ and various optoelectronic applications$^4$–$^5$. These hybrid perovskites have remarkable optoelectronic properties, such as long carrier lifetimes ($\sim 10^2$–$10^3$ ns), high absorption coefficient, high light yield ($\sim 9000$ photons/MeV), large exciton binding energy ($\sim 360$ meV), high carrier mobility, a wide spectral absorption range up to $\sim 800$ nm, long carrier diffusion lengths ($\sim 1$ μm), and low charge carrier recombination rates$^6$–$^8$. Such properties have positioned these materials for various devices, such as solar cells$^9$–$^{10}$, light-emitting diodes$^{11}$, and photodetectors (PDs)$^{12}$–$^{13}$. In just a few years, researchers have found ways to increase the power conversion efficiency of single junction perovskite solar cells to over $\sim 25.5\%$, making it the fastest advancing photovoltaic technology to date$^{10}$. Alongside solar cells, PDs have also attracted significant attention and are finding their way into niche applications, such as optical communications for defense, environmental monitoring, chemical/biological sensing, and space exploration$^{14}$–$^{15}$.

As an optoelectronic device, a PD converts incoming light into a detectable electrical signal through the generation of charge carriers. It is highly desirable that a PD operate at low-power levels, and at the same time exhibit a high photoresponsivity $R$ and detectivity $D$ with a fast response, and a high ratio of photocurrent-to-dark current, i.e., the ON/OFF ratio. The drawback of commercially available PDs based on materials such as SiC, Si, InGaAs, ZnO$^6$–$^{16}$ is their relatively narrow spectral response within the ultra-violet, visible, and infrared regimes, respectively. The hybrid two-dimensional (2D) perovskites when used in PDs have advantages over commercially available PDs, since they exhibit a wide dynamic range given their lower defect densities and tunable bandgaps. External quantum efficiency (EQE) also tends to be impressive over a wide spectral regime$^{16}$. For example, 2D (EDBE)PbCl$_4$ hybrid perovskite (EDBE = $2,2'-(\text{ethylenedioxy})\text{bis}$ (ethyammonium)) has found its way in X-ray detection, likely to replace currently available materials for scintillators, due largely, to the absence of deep traps and a minimal density of shallow trap states within the detector; here thermal artifacts are also nulled-out due to the large exciton binding energy of 2D (EDBE)PbCl$_4$.$^{20}$ The absorption coefficient of the 2D perovskites is also found to be very intimately tied to the direct bandgap nature of the electronic transitions occurring in not only 2D perovskites, but also 3D perovskites$^{12}$. These characteristics strongly suggest that the 2D perovskites are ideal candidates for PDs, particularly since their stability appears to be superior to that of conventional 3D perovskites$^{12}$.

In this paper, 2D $(\text{CH}_3(\text{CH}_2)_3\text{NH}_3)\text{(CH}_3\text{NH}_3)$$_n$$\cdot$$\text{Pb}_x\text{I}_{3n+1}$ family of perovskite compounds ($n = 4$) was synthesized using the Ruddlesden–Popper (RP) method$^{19}$–$^{21}$, which is one of the most common techniques used for the synthesis of 2D perovskites. Previously, a homologous series of RP perovskite phases with the generic formula $(\text{CH}_3(\text{CH}_2)_3\text{NH}_3)\text{(CH}_3\text{NH}_3)$$_n$$\cdot$$\text{Pb}_x\text{I}_{3n+1}$ ($n = 1–7$) were synthesized by Ruddlesden and Popper$^{19}$ using butylammonium as the organic spacer, where the number of layers was adjusted by the ratio between the lead source, the methylammonium iodide (MAI), and the butylamine precursor solutions. As eluded to earlier, the potential of 2D perovskites lies in their enormous structural tunability, which allows flexibility to tailor optoelectronic properties toward a desired application$^{22,24}$. For example, Aharon and Etgar$^{24}$ synthesized highly luminescent

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1Department of Materials Science and Engineering, PACCAR Technology Institute, Denton, TX, USA. 2Department of Electrical Engineering, University of North Texas, Denton, TX, USA. ✉email: anupama.kaul@unt.edu

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MAPbX₃ quantum dots, where the Eₓ varied from ~1.90 to 2.26 eV as the cation X was changed from I⁻ to Br⁻. In particular, n, which is the number of octahedra sheets sandwiched between two organic interlayers, strongly determines the major features of the resulting 2D perovskite, such as bandgap, exciton binding energy, and photoluminescence properties.²⁻³

One of the key parameters to achieving optimal device performance with reference to transduction of incoming light-to-electricity lies in the ability to control charge carrier flow. The electrical contact between the electrode and the active absorber material is known to play a decisive role in influencing carrier transport.⁴⁻⁵ However, fundamental challenges related to contacts often limit the ultimate performance and potential of semiconductors broadly speaking for electronics and optoelectronics, and semiconducting 2D perovskites are no exception. A Schottky barrier Φₛ between the metal and semiconductor often arises, including in transition metal dichalcogenides (TMDCs) based devices,⁶⁻⁷ the TMDCs are a broader class of inorganic layered material, just like hybrid organo-halide 2D perovskites where a weak van der Waals interaction serves as the glue between layers. Schottky barriers significantly limit the injection of charge carriers from the semiconducting transport channel region to the external circuit. Lin et al. thirty-conducted a carrier transport study in single-crystalline CH₂NH₃PbBr₃ perovskites with Φₛ of ~170, 380, and 470 meV for Au, Pt, and Ti electrodes, respectively, where low-power sputtering was used for metal contact deposition. Guo et al. also presented a simulation model of graphene and other metallic van der Waals solids contacting 2D halide perovskite sheets (Cs₂H₂NH₂PbX₃) for field-effect transistors. To date, the few studies that compare multiple contacts to 2D perovskites have exclusively relied on vapor-based techniques such as IPA, to overcome nozzle clogging issues, where a mandatory nozzle cleaning sequence was necessary since the IPA in the Gr/Ag ink dries out quickly. Details on the nozzle cleaning procedure for the Ag/Ag ink is explained in greater detail within the “Methods” section. In Fig. 1c, annealing of the perovskite and Ag/Ag perovskite layers was performed in both cases at 100 °C for 30 min at ambient, where the perovskite layer was annealed first right after printing and then it was placed back into the platen to print the Gr/Ag layers and annealed subsequently. The annealing is critical to drive off entrapped solvents to yield a dense film for realizing high-integrity electronic devices on polyimide (PI) substrates. Our demonstration of successfully printing IPA-based ink dispersions widens the portfolio of other intriguing temperature-sensitive materials that would otherwise be excluded from the portfolio of flexible electronics materials.

RESULTS AND DISCUSSION

Material analysis

In order to construct our devices using the additive manufacturing process of inkjet printing, first, the Gr and Ag inks were formulated using isopropyl alcohol (IPA, 2-propanol) solvent. This is an atypical choice of solvent for inkjet printing, but this choice was necessitated by the constraints of post-processing the underlying 2D perovskite layer upon which the contact layer was printed. Since the perovskite layer degrades at T > 100 °C, low-boiling point solvents used to disperse the 2D metal inks as the contact layer to the underlying perovskite provide the needed advantage during the annealing step to restrict annealing T to < 100 °C. Specifics of the ink formulation steps and the optimized inkjet printing parameters used for printing the perovskite and the contact layers are provided in the “Methods” section. Figure 1 illustrates the complete process flow from a to d. Shown in Fig. 1a, the ink formulation procedure for the 2D perovskite is outlined on the left, while the Gr/Ag ink dispersion chemistry is shown on the right. The inks were formulated using magnetic stirring for the perovskite formulation in dimethylformamide (DMF) (left) and for the Gr/Ag formulation was in IPA using ultrasonication (right). The bottom-left inset in Fig. 1a represents the crystalline structure of the synthesized 2D perovskite (BA₂(MA)₃Pb₄I₁₃) where the BA represents n-butylamine (CH₃(CH₂)₃NH₂) and MA is the methylammonium (CH₃NH₃). The inkjet printing sequence for the heterostructure device architecture is depicted in b, while in c the annealing conditions are shown with the specific temperature constraints. Depicted in Fig. 1d is the final inkjet-printed heterostructure device with the Gr-perovskite and Ag-perovskite shown on the top and bottom, respectively. Figure 1b shows the construction of the inkjet-printed heterostructure perovskite (yellow dispersion) and the Gr/Ag metal contact layer (blue dispersion) devices. Precautionary measures were needed in printing the Gr/Ag dispersions in low-boiling point solvents such as IPA, to overcome nozzle clogging issues, where a mandatory nozzle cleaning sequence was necessary since the IPA in the Gr/Ag ink dries out quickly. Details on the nozzle cleaning procedure for the Ag/Ag ink is explained in greater detail within the “Methods” section. In Fig. 1c, annealing of the perovskite and Gr/Ag layers was performed in both cases at 100 °C for 30 min at ambient, where the perovskite layer was annealed first right after printing and then it was placed back into the platen to print the Gr/Ag layers and annealed subsequently. The annealing is critical to drive off entrapped solvents to yield a dense film for realizing high-integrity electronic devices on polyimide (PI) substrates. Our demonstration of successfully printing IPA-based ink dispersions widens the portfolio of other intriguing temperature-sensitive materials that would otherwise be excluded from the portfolio of flexible electronics materials. Finally, Fig. 1d represents the optical micrograph of the inkjet-printed flexible Gr-perovskite and Ag-perovskite heterostructure PDs on flexible PI substrates with printed Gr (top) and Ag (bottom) contacts, with the perovskite layer beneath the metal contacts.

Charge carrier transport in a perovskite PD is closely influenced by the crystallographic structure and morphology of the photoactive absorber layer to determine device performance.⁸⁻¹⁰ Upon the synthesis of the 2D (CH₃(CH₂)₃NH₂)₃(CH₃NH₃)Pb₄I₁₃ (exact synthesis procedures are outlined in the “Methods” section), XRD of the inkjet-printed perovskite film was performed at room temperature using the Rigaku Ultima III Diffractometer, as shown in Fig. 2a. The sample was a ~15 mm² perovskite pattern printed on top of the PI substrate, as shown in the top-left inset of Fig. 2a. The XRD technique characteristically captures the features of the unit cell crystalline lattice by revealing the specific reflections for the 2D (CH₃(CH₂)₃NH₂)₃(CH₃NH₃)Pb₄I₁₃ perovskite film formed using the RP synthesis approach shown in Fig. 2a. The XRD spectra for the 2D perovskite film displays the typical peaks occurring at 2θ = 13.84° assigned to the (200) (000) and (202) crystallographic plane, while the (111) and (202) reflections reveal the vertical growth morphology of the 2D perovskite with respect to the substrate plane.²² The top-right inset in Fig. 2a shows the low-grazing angle XRD spectra of the same inkjet-printed film taken from 2θ = 2.5° up to 12°. The low-grazing angle XRD reveals the number of layers

npj 2D Materials and Applications (2021) 34

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solution-processed electrical contacts that are compatible with otherwise the key focus of this paper is the breakthrough studies on substrates. by the micrographs in Fig. 2b, c, where the heterostructure PDs (BA)(MA)PbI3, a family of n = 4 2D perovskite compounds, where the BA represents n-butylamine (CH3(CH2)3NH2), and MA is the methylammonium (CH3NH3). inkjet printing of the formulated perovskite (yellow ink) and Gr/Ag (blue ink), to form our heterostructure flexible PD device. Frequent nozzle cleaning is necessary for the Gr/Ag ink as the IPA present in the Gr/Ag ink dries out fast. a Annealing of the perovskite and Gr/Ag layers was performed in both cases at 100 °C for 30 min at ambient, where the perovskite layer was annealed first right after printing and then it was placed back into the platen to print the Gr/Ag layers and an additional annealing step was subsequently conducted. b Optical micrograph of the inkjet-printed flexible Gr-perovskite and Ag-perovskite heterostructure PD devices on flexible PI substrates with printed Gr (top) and Ag (bottom) contacts, where the metal contacts were printed on top of the underlying 2D perovskite layer.

Fig. 1 Complete fabrication process. A complete process flow is shown in this figure that provides a pictorial representation of the ink formulation features in (a), inkjet printing in (b), annealing in (c), and micrographs of fabricated devices in (d). In (a), the perovskite (left) and Gr/Ag inks (right) were formulated using magnetic stirring and ultrasonication, respectively. The details of the ink formulations are explained in the “Methods” section. The bottom-left inset in (a) depicts the crystalline structure of (BA)(MA)PbI3, a family of n = 4 2D perovskite compounds. Three 2D perovskites, which included some 3D n = ∞ phases and other lower RP phases, whereas in n = 7, small amounts of n = 5 and n = 6 co-crystallize. Nonetheless, the key focus of this paper is the breakthrough studies on solution-processed electrical contacts that are compatible with inkjet-printed heterostructure perovskites for PDs on flexible substrates. The inkjet-printed films were imaged using an SEM, as shown by the micrographs in Fig. 2b, c, where the heterostructure PDs were printed on a rigid Si substrate which obviated the need for a conductive coating during SEM imaging. The formation of microfibers within the printed film is clearly evident from this micrograph in Fig. 2b and its inset. This characteristic microfibrillar morphology has been seen in a number of prior studies. Wang et al. reported that a higher PbI2 to MAI ratio (PbI20.8: MA(1)) in the precursor leads to the formation of microfibers within the film, which significantly increases film roughness and yields a very high photoluminescence. In addition, they validated that MAPbI3 resulting from lower PbI2 to MAI ratios (<PbI2(0.6): MA (1)) do not exhibit the typical photoluminescence and absorption peaks. Figure 2c illustrates the 52° tilted top view of the heterostructure PD, where the Gr contacts are apparent on top of the perovskite layer, while its inset on the right displays the magnified view of the printed surface, revealing the embedded network of microfibers and the lateral view of the Gr-perovskite interface.

Electrical transport comparison with Gr and Ag contacts

After completing the material characterization analysis on the synthesized 2D perovskites and fabricating the inkjet-printed PDs, we then proceeded with the electronic and optoelectronic transport measurements at cryogenic temperatures T from ~4 to 350 K using the Lakeshore CRX-4K probe stage and a broadband light source. To compare the Gr and Ag contacts, a systematic study was performed on the inkjet-printed PDs, where a broadband light source was used to illuminate the devices as they were held in vacuum (~10−6 Torr). As mentioned previously, the Gr and Ag contacts are used in this study and both PDs are fabricated using similar conditions for the ink formulation, printing passes, jetting voltage, and annealing temperature, so that a comparative analysis between the two metal contacts is possible. Figure 3a illustrates the distinct T-dependent current (I)–voltage (V) characteristic observed for bias voltages ranging from −40 to +40 V at 10.75 mW/cm² for the Gr-perovskite PD. On the other hand,
Fig. 2  Material characterization. a The XRD spectra of inkjet-printed 2D perovskite films on SiO2/Si substrates. The 20 peaks at 13.84° and 28.31° are assigned to the (CH3(CH2)3NH3)2(CH3NH3)3Pb4I13 (111) and (202) crystallographic planes, respectively. The top-right inset shows low-grazing angle XRD data, that depicts five distinct reflections at ~3.4°, 4.5°, 6.7°, 8.9°, and 10° for 28 < 14° which is indicative of the number of 2D perovskite layers in the compound. The top-left inset displays the optical microscopy image of the printed perovskite sample on top of the PI substrate over an area ~15 mm² used for the XRD analysis. b SEM image of an inkjet-printed perovskite heterostructure PD on a Si substrate. The inset shows the magnified view of the microfibrillar structure of the inkjet-printed 2D perovskites structure, which significantly increases film roughness and yields a very high photoluminescence. c SEM image at 52° tilt angle of the printed Gr-perovskite PD on a Si substrate, where the right inset displays the Gr-perovskite lateral MS junction.

Fig. 3b displays the T-dependent I-V for the Ag-perovskite PD at similar conditions. For both PDs, some nonlinearity in the I-V was observed for T ranging from ~4 to 300 K, and the response appeared to be more Ohmic at T ~350 K. A sudden rise in the photocurrent Ip was observed with respect to T, for both PDs and the results are plotted in Fig. 3c, showing the Ip is increasing as T increases at a fixed light intensity F of ~10.75 mW/cm². At low T, the electrons are localized within their atomic cores, and as T increases, they gain sufficient energy to move from the valence band into the conduction band, forcing Ip to increase as T increases. In Fig. 3c, the Ip rises with T from ~4 to 350 K, particularly at higher T, for both PDs at a fixed bias voltage of ~40 V. While printing both PDs, the number of printing passes and distance between the metal electrodes were kept constant, so relative comparisons in Ip can be made. At 4 K, Ip(~300K) ~4.0 and 3.4 nA, while at 300 K, Ip(~300K) ~14 and 10 nA, for Ag-perovskite and Gr-perovskite, respectively, as summarized in Table 1. The dark current Ip was found to be ~1 pA for both PDs and was T independent, which was measured by turning the broadband light source off. The inset in Fig. 3c shows the Ip behavior over a narrower range from ~4 up to 200 K. At T > 4 K and T > 50 K, the Ip started decreasing until reaching the transition temperature Ttransition ~ 150 and 170 K for Ag-perovskite and Gr-perovskite PDs, respectively; the Ip started to increase rapidly beyond Ttransition. This dip at Ttransition has also been observed in prior reports, where the orthorhombic-to-tetragonal phase transition occurring in 2D perovskites between ~150 and 200 K is noted as the primary cause. Incidentally, Weller et al. established that in CH3NH3PbI3, a low-T orthorhombic-to-tetragonal phase transition is evident at ~165 K, whereas the high-T transition from tetragonal-to-cubic takes place at ~327 K. In the orthorhombic phase (T ~4 K < T < 170 K), where all of the lattice parameters a, b, and c are unequal (a ≠ b ≠ c), a dimensional stress in the unit cell is induced as it transitions to the tetragonal phase, where two of the lattice parameters a and b are equivalent (a = b ≠ c). From the T-dependent I-V of both PDs, the devices contacted with the Ag electrodes clearly showed Ip to be greater for T > 250 K due to the increased collection of photocarriers compared to the Gr contacts. This also supports the Schottky barrier analysis data, which is discussed shortly in reference to Fig. 3f.

To compare the charge transport characteristics of our 2D perovskite with Gr and Ag contacts, the Schottky barrier height ΦB was calculated using T-dependent transport data. Figure 3d, e shows the In(Ip/T²/2) versus 1000/T Arrhenius plot for various V ranging from 0.4 to 4 V for the Gr-perovskite and Ag-perovskite PDs, respectively. The ΦB was extracted from the forward-bias fit for T ~50~300 K using the ideal Schottky diode formula:

\[ I_f = I_s \exp^{\frac{qV_f}{kT}} \]  

(1)

where I_s is defined as forward-bias current, and I_f, the saturation
The current that is given by:

\[ I = A \omega T^2 \exp \left( -\frac{qV_f}{k_B T} \right) \]  

(2)

Here, \( A \) is the Richardson constant, \( \omega \) is the contact area of the metal–perovskite junction, \( q \) is the electron charge (~1.602 \times 10^{-19} \text{ C}), \( V_f \) is the forward-bias voltage, and \( k_B \) is the Boltzmann constant (~8.617 \times 10^{-5} \text{ eV/K}). Since our 2D perovskite falls in the 2D materials family, the \( I_p \) is defined by the 2D thermionic emission equation below\(^{40}\), which employs the reduced power law for a 2D transport channel according to:

\[ I_p = A^{*} \omega T^2 \exp \left[ -\frac{q}{k_B T} \left( \Phi_B - \frac{V}{n} \right) \right] \]  

(3)

Here, \( A^{*} \) is the 2D equivalent Richardson constant, \( n \) is the ideality factor, and \( V \) is the bias voltage. The \( \Phi_B \) was extracted from the \( \ln(I_p/T^{3/2}) \) versus 1000/T at bias voltages ranging from 0.4 to 4 V for Gr-perovskite and Ag-perovskite PDs. At 0 V, the \( \Phi_B \) was found to be ~920 and 712 meV for Gr-perovskite and Ag-perovskite PDs, respectively, in the \( T \) regime from ~100 to 150 K.
almost saturates above 1 V for both PDs. At 0 V, the $\Phi_B$ was found to be $\sim 920$ and 712 meV for Gr-perovskite and Ag-perovskite, respectively, in the T regime from $\sim 50$ to 100 K. Table 1 summarizes the $\Phi_B$ of our inkjet-printed perovskite with Gr and Ag contacts. For our synthesized perovskite, the experimental value of $\Phi_B$ was compared with the theoretical equivalent, where $\Phi_B$ (theoretical) was determined using:

$$\Phi_B(\text{theoretical}) = \Phi_{\text{metal}} - \chi$$  (4)

The calculated theoretical $\Phi_B$ values were determined to be $\sim 680$ and 440 meV for Gr-perovskite and Ag-perovskite interfaces, respectively, where the work function $\phi$ of Gr and Ag are $\phi_{\text{Gr}} = 4.5$ eV and $\phi_{\text{Ag}} = 4.26$ eV, respectively, and the perovskite electron affinity $\chi \approx 3.82$ eV.\(^\text{42}\). The difference between the theoretical $\Phi_B$ of the two contact metals is $\Delta \Phi_B(\text{theoretical}) = \Phi_B(\text{Gr}) - \Phi_B(\text{Ag}) = 680 - 440 = 240$ meV, whereas at a 0 V bias voltage, the difference between the experimental $\Phi_B$ values is $\Delta \Phi_B(\text{experimental}) = \Phi_B(\text{Gr}) - \Phi_B(\text{Ag}) = 920 - 712 = 208$ meV, which closely matches $\Delta \Phi_B(\text{theoretical})$. In both the theoretical and experimental cases, $\Phi_B$ for Ag was found to be lower than that of the Gr contact. This is in alignment with the higher $I_p$ observed in our Ag-contacted 2D perovskite devices, in contrast to the Gr contacted devices. Limited prior studies exist on contacts to 2D perovskites using vaporization-assisted metal contact deposition\(^\text{31}\), where $\Phi_B$ was found to be $\sim 170$, 380, and 470 meV for Au, Pt, and Ti electrodes, respectively. All our inkjet-printed electrical contacts yield a facile, reliable, and more cost-effective route to form electrical contacts to 2D perovskites, which should pave the way for their future applications in optoelectronics and photovoltaics.

To fully characterize the performance of our inkjet-printed PDs, their figures of merit were computed, such as $R$, $D$, EQE, ON/OFF ratio, and wavelength $\lambda$-dependent transport, as shown by the data in Fig. 4a-d. Figure 4a provides the dependence of $R$ as a function of light intensity $F$ for both Gr- and Ag-contacted PDs at $T \sim 300$ K and biased at 40 V. Here, the $R$ is determined using:

$$R = \frac{I_{ph}}{F}$$  (5)

with $I_{ph}$ as the photocurrent density in A/cm$^2$ and $F$ as the light intensity in W/cm$^2$. From Fig. 4a, the $R$ was calculated to be $\sim 0.27$ and 0.53 A/W for the Gr-perovskite and Ag-perovskite PDs, respectively, at $F \sim 5.24 \mu$W/cm$^2$ ($0.00524$ mW/cm$^2$) and a decrease is noted at higher $F$ for both PDs. Similarly, at $T \sim 300$ K, the inset in Fig. 4a shows the corresponding $D$ as a function of $F$ for both PDs at 40 V, where the $D$ is tabulated using:

$$D = \frac{\omega^{1/2} R}{(2q\rho s)^{1/2}}$$  (6)

here $D$ is measured in cm Hz$^{1/2}$/W$^{-1}$ (Jones), $\omega$ is the effective area ($\sim 0.0048$ cm$^2$) between the metal contacts, $R$ is the responsivity, and $I_p$ is the dark current ($\sim 4$ pA) in Amps. At 300 K and $F = 5.24$ $\mu$W/cm$^2$ ($0.00524$ mW/cm$^2$), $D$ was calculated to be $\sim 1.55 \times 10^{-13}$ Jones and $3.24 \times 10^{-13}$ Jones for the Gr-perovskite and Ag-perovskite PDs, respectively. It is seen that for the Ag-perovskite PD, both the $R$ and $D$ are 2X higher compared to the Gr-perovskite PDs. Table 1 summarizes the $R$ and $D$ of our inkjet-printed perovskite with Gr and Ag contacts. The $R$ for Ag-perovskite is higher compared to other heterostructure PDs, where the perovskite was contacted with thermally evaporated Au and ITO\(^\text{42,43}\). In particular, the Au/CH$_3$NH$_3$PbI$_3$/ITO PDs showed lower $\sim 0.036$ and 0.037 A/W, respectively, whereas Au/CH$_3$NH$_3$PbI$_3$/Au PDs demonstrated higher $\sim 10.33$ A/W;\(^\text{42}\) interestingly the CH$_3$NH$_3$PbI$_3$ nanonets were created using monolayer colloidal crystal templates. Additionally, 3D perovskites with Au contacts\(^\text{45,46}\) also showed lower $R$ and $D$ compared to our Ag-perovskite PDs. Other combinations of electrode–absorber heterostructures include Pt/MAPbCl$_3$/Ti/Au\(^\text{47}\) and Au/MAPbI$_3$ PDs\(^\text{48}\), which display lower $R = 0.0469$ and 0.10 A/W, respectively, while the Pt/MAPbCl$_3$/Ti/Au\(^\text{46}\) and Au/MAPbI$_3$\(^\text{47}\) showed $10^3$ X lower values of $D$ compared to the Ag-perovskide PD demonstrated here.

Figure 4b displays the EQE obtained for both PDs as a function of $T$ at $F = 5.24$ $\mu$W/cm$^2$ ($0.00524$ mW/cm$^2$). The EQE is defined as the number of electron–hole pairs generated for an incident photon impinging onto the PD, and takes the following form:

$$EQE = \frac{R}{\hbar c} \frac{h c}{\lambda q}$$  (7)

where $h \sim 6.6 \times 10^{-34}$ J s is Planck’s constant, and all the other variables are as denoted previously with $\lambda \sim 630$ nm for the laser source used. The EQE seems to increase with increasing $T$ for both PDs, reaching $\sim 78$% and $103$% at $\sim 300$ K for the Gr-perovskite and Ag-perovskite, respectively. High EQE values have previously been reported for WSe$_2$, graphene/Si, and Ge-Si based PDs. The situation of EQE exceeding 100% arises as charge traps localize the photogenerated carriers, increasing their lifetime and results in their recirculation multiple times before recombination. With this gain mechanism, a higher responsivity and EQE often result\(^\text{50}\). The inset in Fig. 4b shows the EQE as a function of $F$, where the EQE decreases with increasing $F$. At $F = 5.24$ $\mu$W/cm$^2$ ($0.00524$ mW/cm$^2$), the EQE = 103%, whereas at $F = 10.75$ mW/cm$^2$, the EQE decreased dramatically to $\sim 0.05$% for the Ag-perovskite PD. Figure 4c displays the ON/OFF ratio for the Gr-perovskite and Ag-perovskite

### Table 1. Comparison of photocurrent $I_p$ barrier height $\Phi_B$, photoresponsivity $R$, detectivity $D$, rise time $\tau_{\text{rise}}$, fall time $\tau_{\text{fall}}$, ON–OFF ratio, and external quantum efficiency (EQE) of Gr-perovskite and Ag-perovskite flexible PDs at room T.

| Device architecture | $I_p$ (nA) | $\Phi_B$ (meV) | $R$ (A/W) | $D$ (Jones) | $\tau_{\text{rise}}$/$\tau_{\text{fall}}$ (ms) | ON–OFF ratio | EQE (%) | References |
|---------------------|-----------|---------------|-----------|-------------|------------------------------------------|-------------|---------|------------|
| Gr-(BA)$_2$(MA)$_3$Pb$_4$I$_3$ | 0.3 at 1 V | 920 | 0.27 | $1.55 \times 10^{13}$ | 31, 27 | $2 \times 10^3$ | 78 | This work |
| Ag-(BA)$_2$(MA)$_3$Pb$_4$I$_3$ | 0.4 at 1 V | 712 | 0.53 | $3.24 \times 10^{13}$ | 17, 45 | $3.4 \times 10^3$ | 103 | This work |
| Au/CH$_3$NH$_2$PbBr$_3$ | 170 | | | | | | | 31 |
| Pt/CH$_3$NH$_2$PbI$_3$ | 380 | | | | | | | 44 |
| Ti/CH$_3$NH$_2$PbBr$_3$ | 470 | | | | | | | 47 |
| Au/CH$_3$NH$_2$PbI$_3$/ITO | 8 at 1 V | 0.036 | 5 $\times 10^{10}$ | 150, 53 | 6 $\times 10^2$ | 100 | 51 |
| Au/CH$_3$NH$_2$PbI$_3$ | 200 at 0.1 V | 0.055 | | | | | | 42 |
| Au/CsPbBr$_3$ | 1.1 at 1 V | 17.8, 14.7 | | | | | | 51 |
| polycrystalline $\alpha$-FAPbI$_3$ | 0.95 | $2.8 \times 10^{12}$ | 12.4, 17.8 | | | | | 182 |

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npj 2D Materials and Applications (2021) 34

R.F. Hossain et al.
PDs for $T$ ranging from ~4 to 350 K, which establishes an important figure-of-merit that is defined as the “ON” state referring to the collected current under illumination, and the “OFF” state referring to the current in the dark. As seen from Fig. 4c, the “ON/OFF” ratio increased with increasing $T$ for both PDs, although at $T$ ~4 – 170 K, the ON/OFF ratio decreased due to the orthorhombic-to-tetragonal phase transition explained in reference to the data in Fig. 3c. At ~300 K, the ON/OFF ratios were found to be $\sim 2 \times 10^3$ and $3.4 \times 10^3$ for the Gr-perovskite and Ag-perovskite PDs, respectively, which supports our previous results on the lower Schottky barrier height calculated for the Ag contacts. Table 1 summarizes the ON/OFF ratios of our inkjet-printed perovskite with Gr and Ag contacts. The high ON/OFF ratios of $\sim 3.4 \times 10^3$ obtained for the Ag-perovskite PDs are at least $\sim 30$ X higher compared to prior PD reports based on other perovskites, such as CH$_3$NH$_3$PbI$_3$ $^{54, 47}$ and CsPbBr$_3$ $^{51}$, where the ON/OFF ratios reported were $\sim 10^3$. In yet other similar studies, where polycrystalline α-FAPbI$_3$ $^{52}$ were used to fabricate PDs, the ON/OFF ratios obtained were somewhat higher $\sim 8.6 \times 10^4$.

We also conducted additional optoelectronic measurements on our PD devices using a tunable fiber-coupled laser source from NKT Photonics (part #: A371-200-000 and A371-500-000), where $\lambda$ was varied from 400 to 2300 nm. The filters were switched between the measurements due to the restriction in ranges (400–1000 nm, Filter- M00010357; 1000–2300 nm, Filter-M00010266). Figure 4d exhibits the $I_p$ versus $\lambda$ plot for the Gr-perovskite PD at $T$ ~200, 300, and 350 K, while the inset shows the corresponding $I_p$ versus $\lambda$ for the Ag-Perovskite PD at $T$ ~200, 300, and 350 K.

Figure 5a, b displays the temporal response of $I_p$ to ON/OFF optical radiation pulses at $T$ ~100, 200, 300, and 350 K with $F$ ~10.75 mW/cm$^2$ for the Gr-perovskite and Ag-perovskite PDs, respectively. Figure 5c, d exhibit the photovoltaic characteristics of the Gr-perovskite and Ag-perovskite PDs, respectively.
Thorlabs DC2200 pulse modulator for the broadband light source, where the pulse width was fixed at 500 ms. The rise and decay of $I_p$ is governed by trap states and recombination dynamics within the perovskite, and this temporal response thus serves as a gauge, to first order, to shed insights on the degree to which trap states influence photo-induced carrier dynamics. A good photosensitive material, such as a perovskite not only shows a high $I_p$ during the "ON" state, but it also yields a fast response time to the incoming radiation, as our measurements reveal. If the carrier dynamics are influenced by defects that serve as trapping centers, the response time is typically much slower. In Fig. 5a, b, a fast increase and fast decay of $I_p$ were observed with good repeatability, followed by the saturation of $I_p$ during the "ON" state, but it also yields a fast response time to the incoming radiation, as our measurements reveal. The rise time $\tau_{rise}$ and fall time $\tau_{fall}$ are defined as the time it takes for the PD to reach 90% and drop to 10% of the maximum steady-state $I_p$, respectively. At ~300 K, $\tau_{rise}$ ~31 ms and $\tau_{fall}$ ~27 ms were determined for the Gr-perovskite PD, while $\tau_{rise}$ ~17 ms and $\tau_{fall}$ ~45 ms were measured for the Ag-perovskite PD. Our data reveal that the Ag-perovskite PD is at least 8 X faster compared to some previous reports where evaporated Au served as the metal contact to CH$_3$NH$_3$PbI$_3$ PD devices. Table 1 summarizes the $\tau_{rise}$ and $\tau_{fall}$ of our inkjet-printed 2D perovskite PD devices contacted with solution-processed Gr and Ag, along with a comparison of other figures of merits for PD to prior studies. While the fast photocurrent rise is attributed to the initial equilibration of photocarrier generation and recombination rates, the fast decay is due to the recombination of free carriers. For both PDs, the $\tau_{rise}$ and $\tau_{fall}$ seem to decrease nonlinearly with increasing $T$, although the $\tau_{fall}$ for the Ag-perovskite PD at ~300 K seems to increase compared to the $\tau_{rise}$, which suggests that recombination of the photocarriers occurs over a longer duration at room $T$ for the Ag-perovskite. Generally, the values of $\tau_{rise}$ and $\tau_{fall}$ were lowest for $T$ ~100 up to 150 K for both PDs, which is intriguing and may likely be associated with the orthorhombic-to-tetragonal crystal phase transition occurring in 2D perovskites within this temperature regime, as discussed previously. The transients appear to be faster within this temperature range due possibly to the structural changes occurring within the 2D perovskite absorber layer, where carrier effective masses are likely to change from the crystalline phase transformation, which will influence switching speeds.

**Strain-dependent photoresponse of Ag-perovskite PD**

Strain engineering has been broadly applied to semiconducting materials, such as Si with the addition of Ge, to achieve high switching speed transistors with both compressive and tensile strain. As the Ag-perovskite PD showed superior performance compared to the Gr-perovskite PDs, we then performed mechanical durability tests on the Ag-perovskite PD. The mechanical bending tests were carried out using 3D printed structures constructed at five different radii of curvatures: 0.072, 0.087, 0.112, 0.157, and 0.262 cm$^{-1}$. The experiment was performed under a...
bias voltage of ~20 V, and the \( I_p \) response was measured as a function of strain with varying light intensity. Figure 6a displays the five repetitive cycles of \( I_p \) measured as a function of \( F \) on a flat surface. In the first cycle, \( F \) was increased from \( ~58 \mu \text{W/cm}^2 \) up to the maximum of \( 32 \text{ mW/cm}^2 \) with a time delay of 5 s in between each incremental \( F \) to stabilize the response. The \( F \) was then lowered from \( ~32 \text{ mW/cm}^2 \) back down to \( ~58 \mu \text{W/cm}^2 \), prior to initiating the second measurement cycle, all on a flat surface. As seen in Fig. 6a, there is no significant change in the \( I_p \) at low \( F \sim 58 \mu \text{W/cm}^2 \) and 20 V, while at higher \( F \), the \( I_p \) increased, likely due to electrical annealing of the contacts and the film, which requires further investigation in the future to better understand the underlying phenomenon. The increase in \( I_p \) was tabulated to be \( ~57\% \), 26\%, 21\%, 16\%, and 12\% for \( F \) = 1.2, 8.2, 18.9, 26.8, and 32 mW/cm\(^2\), respectively, which indicates a gradual reduction in the net percent increase as \( F \) increases.

Figure 6b displays the schematic diagram of the strained flexible Ag-perovskite PD while under illumination. Figure 6c shows the \( I_p \) versus \( F \) as a function of strain for all the five curvatures tested, where the increase in \( I_p \) is consistent with increasing \( F \) over all the curvatures. Similarly, the \( I_p \) dependency with curvature at various \( F \) is illustrated in Fig. 6d, and it is apparent that the \( I_p \) decreases with increasing strain levels over the range of \( F \) used. The strain causes mechanical deformation and produces piezoelectric charges in the perovskite at the heterojunction interface. The electric field at the interface and the increased MS junction effective area provides a smaller driving force to separate the photogenerated electron–hole pairs, which reduces \( I_p \). Also, Zhang et al.\(^{56} \) have discussed that the external strain also possibly changes the Pb–I bond lengths, the Pb–I–Pb bond angles, and the orientations of the CH\(_3\)NH\(_3\)\(^+\) molecules, and these strain-induced structural variations in the crystalline order result in reduced photocarrier generation. Their studies\(^{56} \) also shed insights on the photovoltaic properties of CH\(_3\)NH\(_3\)PbI\(_3\) under external strain, where the absorption efficiency of incoming photons was lower.

In summary, we have synthesized (CH\(_3\)\(_2\))\(_2\)(CH\(_3\)NH\(_3\))\(_2\)(CH\(_3\)NH\(_3\))\(_{n-1}\) Pb\(_n\)I\(_{3n-1}\) (\( n = 4 \)) family of 2D perovskites and characterized their properties using XRD (including at low-grazing angles) and SEM. Contact engineering of 2D layered perovskites is presented with Gr and Ag metals, where inkjet printing was used to fabricate heterostructure flexible PD devices on PI substrates. The \( \Phi_p \) for our Gr-perovskite and Ag-perovskite PDs was extracted to be ~920 and 712 meV, respectively, in the \( T \) regime from ~100 to 150 K. The measured \( R \) and \( D \) for the Gr-perovskite and Ag-perovskite PDs confirmed the higher \( R \sim 0.53 \text{ A/W} \) and \( D \sim 3.24 \times 10^{13} \) Jones for the Ag-contacted 2D perovskite. Similarly, the EQE was found to be higher for Ag-perovskite when compared to Gr-perovskite PD. The ON/OFF ratio and response times, \( t_{\text{rise}} \) and \( t_{\text{fall}} \) for the Ag-perovskite PD were at least 30 X and 8 X higher, respectively, compared to prior reports. The \( \lambda \)-dependent \( I_p \) measurement revealed that the maximum \( I_p \) occurred at \( \lambda \sim 630 \) nm for both types of devices, which is consistent with the energy bandgap of the 2D perovskite of our \( n = 4 \) formulation. Lastly, strain-dependent bending tests showed the modulation of \( I_p \) as a function of strain. The study presented here validates the
importance of contacts to influence charge carrier dynamics, and our exceptional figures of merits particularly with inkjet-printed Ag contacts to 2D perovskites suggests that our solution-processed 2D perovskites are well-positioned to have a significant impact on flexible optoelectronics and flexible PV research in the future.

METHODS

Synthesis of the 2D perovskite crystal
We synthesized the \((\text{CH}_3\text{NH}_3)_2\text{Pb}_4\text{I}_{13}\) perovskite, which is a family of layered compounds with tunable semiconducting properties. The PbO \((\text{part #: 402982})\), HI \((\text{part #: 210021})\), H₂PO₂ \((\text{part #: 214906})\), and n-CH₃(CH₂)₃NH₂ \((\text{part #: 471305})\) were purchased from Sigma-Aldrich. The PbO powder \((2232 \text{ mg})\) was dissolved in a mixture of 57% w/v aqueous HI solution \((10.0 \text{ mL})\) and 50% aqueous H₂PO₂ \((1.7 \text{ mL})\) by heating at 130 °C and subsequent boiling under constant magnetic stirring of 350 rpm for about 25 min, that led to the formation of a bright yellow solution. Subsequent addition of solid CH₃NH₃I \((507 \text{ mg})\) to the hot yellow solution initially caused the precipitation of a black powder that rapidly redissolved under stirring to afford a clear bright yellow solution. Additionally, the n-CH₃(CH₂)₃NH₂ \((248 \mu\text{L})\) and hydriodic acid \((5 \text{ mL})\) were mixed separately in a glass vial and the mixture was then added dropwise to the solution under vigorous stirring for 10 min, which did not result in any visible changes to the solution. After 10 min, we stopped stirring and heating, which were previously at 350 rpm and 130 °C, respectively. The solution was left to cool to room temperature during which time deep black, rectangular-shaped platelets started to crystallize. The precipitation was deemed to be complete after ~2 h. The crystals were isolated by suction filtration and thoroughly dried under reduced pressure."
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ADDITIONAL INFORMATION

Correspondence and requests for materials should be addressed to A.B.K.

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