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

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Silver (Ag) and graphene (Gr) inks have been engineered to serve as efficient electrical contacts for solution-processed two-dimensional (2D) organo-halide $(\text{CH}_3(\text{CH}_2)_3\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_{n-1}\text{PbI}_{3n+1}$ ($n = 4$) 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 λ -dependent photocurrent I_p peaked at $\lambda \sim 630$ nm for both PDs, consistent with the bandgap $E_g \sim 1.96$ 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 ABX_3 ($A = \text{CH}_3\text{NH}_3^+$; $B = \text{Pb}^{2+}$ or Sn^{2+} ; and $X = \text{Cl}^-$, I^- , 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 (~ 9000 photons/MeV), large exciton binding energy (~ 360 meV), high carrier mobility, a wide spectral absorption range up to ~ 800 nm, long carrier diffusion lengths (~ 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 diodes¹¹, 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 date¹⁰. 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^{16–18} 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 regime¹⁹. For example, 2D (EDBE)PbCl₄ hybrid perovskite (EDBE = 2,2'-(ethylenedioxy)bis(ethylammonium)) 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)PbCl₄²⁰. 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 perovskites¹². 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 perovskites¹².

In this paper, 2D $(\text{CH}_3(\text{CH}_2)_3\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_{n-1}\text{PbI}_{3n+1}$ family of perovskite compounds ($n = 4$) was synthesized using the Ruddlesden–Popper (RP) method^{19,21,22}, 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 $(\text{CH}_3(\text{CH}_2)_3\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_{n-1}\text{PbI}_{3n+1}$ ($n = 1$ – 7) were synthesized by Ruddlesden and Popper¹⁹ 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^{23,24}. For example, Aharon and Etgar²⁴ synthesized highly luminescent

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MAPbX₃ quantum dots, where the E_g 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 properties²³.

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 transport²⁵. 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 Φ_B between the metal and semiconductor often arises, including in transition metal dichalcogenides (TMDCs) based devices^{26,27}; the TMDCs are a broader class of inorganic layered materials^{28–30}, 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.³¹ conducted a carrier transport study in single-crystalline CH₃NH₃PbBr₃ perovskites with Φ_B 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.³² also presented a simulation model of graphene and other metallic van der Waals solids contacting 2D halide perovskite sheets (C₄H₉NH₃)₂PbX₄ (X = Cl, Br, and I) for field-effect transistors. To date, the few studies that compare multiple contacts to 2D perovskites have exclusively relied on vapor-based techniques^{31,32}. However, vapor-based techniques are very expensive, time-consuming, and require specialized equipment for the metal contact deposition.

In this report, we provide prototypical demonstrations of inkjet printed, solution-processed electrical contacts to inkjet-printed 2D perovskites formed on flexible substrates. Our devices were constructed with the 2D perovskite serving as the optical absorber layer in a PD platform. The metal contacts explored here include inkjet-printed graphene (Gr) with work function $\phi_{Gr} \sim 4.5$ eV, and inkjet-printed silver (Ag) with work function $\phi_{Ag} \sim 4.26$ eV, where efficient carrier injection from the 2D perovskite to the external contacts at the metal–semiconductor (MS) interface is validated through temperature T -dependent and wavelength λ -dependent optoelectronic transport measurements of the photocurrent I_p ; from these measurements Φ_B was then extracted. Besides material characterization conducted on our 2D (CH₃(CH₂)₃NH₃)₂(CH₃NH₃) _{$n-1$} Pb _{$n+1$} ($n=4$) formulations using techniques such as x-ray diffraction (XRD), including at low-grazing angles ($\theta = 2.5^\circ$ – 12°), and scanning electron microscopy (SEM), the device figures of merit, such as R and D , ON/OFF ratio, τ_{rise} and τ_{fall} , EQE were calculated for both the Gr and the Ag-contacted PDs. Additionally, the λ -dependent I_p and strain-dependent bending measurements were also performed. Our promising results, particularly with Ag contacts, confirm the excellent potential of inkjet-printed 2D perovskites for enabling high-performance PDs on flexible substrates using scalable, additive manufacturing production routes for flexible electronics and solar cells in the future.

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 $T > 100^\circ\text{C}$ ³³, 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 $<100^\circ\text{C}$. 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 (BA)₂(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 Gr/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 performance³⁴. Upon the synthesis of the 2D (CH₃(CH₂)₃NH₃)₂(CH₃NH₃)₃Pb₄I₁₃ (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)₃NH₃)₂(CH₃NH₃)₃Pb₄I₁₃ perovskite film formed using the RP synthesis approach^{19,21}. The XRD spectra for the 2D perovskite film displays the typical peaks occurring at $2\theta = 13.84^\circ$ assigned to the (CH₃(CH₂)₃NH₃)₂(CH₃NH₃)₃Pb₄I₁₃ (111) crystallographic planes²¹. Additionally, the 2θ peaks at 27.23° and 28.31° are assigned to the (0k0) and (202) crystallographic plane, while the (111) and (202) reflections reveal the vertical growth morphology of the 2D perovskite with respect to the substrate plane²². The top-right inset in Fig. 2a shows the low-grazing angle XRD spectra of the same inkjet-printed film taken from $2\theta = 2.5^\circ$ up to 12° . The low-grazing angle XRD reveals the number of layers

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 $(\text{BA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13}$, a family of $n = 4$ 2D perovskite compounds, where the BA represents *n*-butylamine ($\text{CH}_3(\text{CH}_2)_3\text{NH}_2$), and MA is the methylammonium (CH_3NH_3). **b** 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. **c** 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. **d** 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.

present in the 2D perovskite³⁵, and is evident from the top-right inset of Fig. 2a, five distinct reflections for $2\theta < 14^\circ$ are identified, which occur at $\sim 3.4^\circ$, 4.5° , 6.7° , 8.9° , and 10° ; this is indicative of the number of PbI_3 octahedra present in each layer of the 2D perovskite crystal. Although our synthesized 2D perovskite was experimentally designed to have four layers (i.e., $n = 4$) according to the RP synthesis approach, the low-grazing XRD spectra suggests that there may be an additional layer within the compound, which nonetheless is still a 2D perovskite^{19,21,35}, though impurities may also cause this. Ruddlesden and Popper¹⁹ also indexed an additional peak in their XRD scan for 2D $(\text{CH}_3(\text{CH}_2)_3\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_{n-1}\text{Pb}_n\text{I}_{3n+1}$ ($n = 6$), which included some 3D $n = \infty$ 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^{36–38}. Wang et al.³⁸ reported that a higher PbI_2 to MAI ratio ($>\text{PbI}_2(0.8)$: 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 MAPbI_3 resulting from lower PbI_2 to MAI ratios ($<\text{PbI}_2(0.6)$: MA(1)) do not exhibit the typical photoluminescence and absorption peaks³⁸. 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 ($\sim 10^{-6}$ 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/cm^2 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 2θ 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 $2\theta < 14^\circ$ 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 microfibular structure of the inkjet-printed 2D perovskites structure, which significantly increases film roughness and yields a very high photoluminescence³⁸. **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 $T \sim 350$ K. A sudden rise in the photocurrent I_p was observed with respect to T , for both PDs and the results are plotted in Fig. 3c, showing the I_p 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 I_p to increase as T increases. In Fig. 3c, the I_p 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 I_p can be made. At 4 K, $I_{p(4K)} \sim 4.0$ and 3.4 nA, while at 300 K, $I_{p(300K)} \sim 14$ and 10 nA, for Ag-perovskite and Gr-perovskite, respectively, as summarized in Table 1. The dark current I_d 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 I_p behavior over a narrower range from ~4 up to 200 K. At $T > 4$ K and $T > 50$ K, the I_p started decreasing until reaching the transition temperature $T_{\text{transition}} \sim 150$ and 170 K for Ag-perovskite and Gr-perovskite PDs, respectively; the I_p started to increase rapidly beyond $T_{\text{transition}}$. This dip at $T_{\text{transition}}$ 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 cause³⁹. Incidentally, Weller et al.³⁹ 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 ($T \sim 4$ K < T < 170 K), where all of the lattice parameters a , b , and c are unequal ($a \neq b \neq c$), 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 ($a = b \neq c$). From the T -dependent I - V of both PDs, the devices contacted with the Ag electrodes clearly showed I_p 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 Φ_B was calculated using T -dependent transport data. Figure 3d, e shows the $\ln(I_p/T^{3/2})$ 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 Φ_B was extracted from the forward-bias fit for $T \sim 50$ –300 K using the ideal Schottky diode formula:

$$I_f = I_s \exp^{qV_f/k_B T} \quad (1)$$

where I_f is defined as forward-bias current, and I_s the saturation

Fig. 3 Electronic and optoelectronic transport data of the 2D perovskite PD. The I - V characteristics of **a** Gr-perovskite and **b** Ag-perovskite heterostructure PDs with T ranging from ~ 4 to 350 K at $F \sim 10.75 \text{ mW/cm}^2$. **c** The T -dependent I_p change of Gr-perovskite and Ag-perovskite PDs for T ranging from ~ 4 to 350 K. The inset displays the I_p behavior for T ranging from ~ 4 to 200 K, where the $T_{\text{transition}}$ was observed at ~ 150 and 170 K for Gr-perovskite and Ag-perovskite PDs, respectively, which is likely due to the orthorhombic-to-tetragonal phase transition occurring within the perovskite. The Arrhenius plot of $\ln(I_p/T^{3/2})$ versus $1000/T$ at bias voltages ranging from 0.4 to 4 V for **d** Gr-perovskite and **e** Ag-perovskite PDs. **f** The Schottky barrier height Φ_B as a function of voltage for the Gr-perovskite and Ag-perovskite PDs. At 0 V, the Φ_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.

current that is given by:

$$I_s = A\omega T^2 \exp^{-q\Phi_B/k_B T} \quad (2)$$

here A is the Richardson constant, ω is the contact area of the metal-perovskite junction, q is the electron charge ($\sim 1.602 \times 10^{-19} \text{ C}$), V_f is the forward-bias voltage, and k_B is the Boltzmann constant ($\sim 8.617 \times 10^{-5} \text{ eV/K}$). Since our 2D perovskite falls in the 2D materials family, the I_p is defined by the 2D thermionic emission equation below⁴⁰, which employs the reduced power

law for a 2D transport channel according to:

$$I_p = A^* \omega T^3 \exp \left[-\frac{q}{k_B T} (\Phi_B - V) \right] \quad (3)$$

here A^* is the 2D equivalent Richardson constant, n is the ideality factor, and V is the bias voltage. The Φ_B was extracted from the $\ln(I_p/T^{3/2})$ versus $1000/T$ Arrhenius plot in the T regime from ~ 100 to 150 K through the linear fit $y = a + bx$, where b is the slope and a is the y-intercept. Figure 3f displays the change in Φ_B with increasing bias voltage. It is observed that at 0.4 V, the Φ_B decreased more than half of its initial value at 0 bias voltage and

Table 1. Comparison of photocurrent I_p , barrier height Φ_B , photoresponsivity R , detectivity D , rise time τ_{rise} and fall time τ_{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)	Φ_B (meV)	R (A/W)	D (Jones)	τ_{rise} τ_{fall} (ms)	ON–OFF ratio	EQE (%)	References
Gr-(BA) ₂ (MA) ₃ Pb ₄ I ₁₃	0.3 at 1 V	920	0.27	1.55×10^{13}	31, 27	2×10^3	78	This work
Ag-(BA) ₂ (MA) ₃ Pb ₄ I ₁₃	0.4 at 1 V	712	0.53	3.24×10^{13}	17, 45	3.4×10^3	103	This work
Au/CH ₃ NH ₃ PbBr ₃		170						31
Pt/CH ₃ NH ₃ PbBr ₃		380						
Ti/CH ₃ NH ₃ PbBr ₃		470						
Au/CH ₃ NH ₃ PbI ₃ /ITO	8 at 1 V		0.036					44
Au/CH ₃ NH ₃ PbI ₃	200 at 0.1 V		0.055	5×10^{10}	150, 53	6×10^2		47
Au/CsPbBr ₃	1.1 at 1 V				17.8, 14.7	100		51
polycrystalline α -FAPbI ₃			0.95	2.8×10^{12}	12.4, 17.8	8.6×10^4	182	52

almost saturates above 1 V for both PDs. At 0 V, the Φ_B was found to be ~ 920 and 712 meV for Gr-perovskite and Ag-perovskite, respectively, in the T regime from ~ 50 to 100 K. Table 1 summarizes the Φ_B of our inkjet-printed perovskite with Gr and Ag contacts. For our synthesized perovskite, the experimental value of Φ_B was compared with the theoretical equivalent, where Φ_B (theoretical) was determined using:

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

The calculated theoretical Φ_B values were determined to be ~ 680 and 440 meV for Gr-perovskite and Ag-perovskite interfaces, respectively, where the work function ϕ of Gr and Ag are $\phi_{\text{Gr}} = 4.5$ eV and $\phi_{\text{Ag}} = 4.26$ eV, respectively, and the perovskite electron affinity $\chi \sim 3.82$ eV⁴¹. The difference between the theoretical Φ_B of the two contact metals is $\Delta\Phi_B(\text{theoretical}) = \Phi_B(\text{Gr}) - \Phi_B(\text{Ag}) = 680 - 440$ meV = 240 meV, whereas at a 0 V bias voltage, the difference between the experimental Φ_B values is $\Delta\Phi_B(\text{experimental}) = \Phi_B(\text{Gr}) - \Phi_B(\text{Ag}) = 920 - 712$ meV = 208 meV, which closely matches $\Delta\Phi_B(\text{theoretical})$. In both the theoretical and experimental cases, Φ_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 evaporation-assisted metal contact deposition³¹, where Φ_B was found to be ~ 170 , 380 , and 470 meV for Au, Pt, and Ti electrodes, respectively. Our all inkjet-printed electrical contacts yield a facile, reliable, and more cost-effective route to form electrical contacts to 2D perovskites, which resulted in $\Phi_B \sim 712$ meV for the MS junction interface with Ag-perovskite. This work shows the important steps toward the analysis of the Schottky barrier between inkjet-printed Gr and Ag 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 λ -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:

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

with J_{ph} as the photocurrent density in A/cm² and F as the light intensity in W/cm². From Fig. 4a, the R was calculated to be ~ 0.27 and 0.53 A/W for the Gr-perovskite and Ag-perovskite PDs, respectively, at $F \sim 5.24$ $\mu\text{W}/\text{cm}^2$ (0.00524 mW/cm²) 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:

$$D = \frac{\omega^{1/2} R}{(2qI_d)^{1/2}} \quad (6)$$

here D is measured in cm Hz^{1/2} W⁻¹ (Jones), ω is the effective area (~ 0.0048 cm²) between the metal contacts, R is the responsivity, and I_d is the dark current (~ 4 pA) in Amps. At 300 K and $F \sim 5.24$ $\mu\text{W}/\text{cm}^2$ (0.00524 mW/cm²), D was calculated to be $\sim 1.55 \times 10^{13}$ Jones and 3.24×10^{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 $2\times$ 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^{42,43}. In particular, the Au/CH₃NH₃PbI₃/ITO⁴⁴ and CH₃NH₃PbI₃/Au⁴² PDs showed $R \sim 0.036$ and 0.037 A/W, respectively, whereas Au/CH₃NH₃PbI₃ nanonet PD demonstrated higher $R \sim 10.33$ A/W⁴³; interestingly the CH₃NH₃PbI₃ nanonets were created by using monolayer colloidal crystal templates. Additionally, 3D perovskites with Au contacts^{45,46} also showed lower R and D compared to our Ag-perovskite PDs. Other combinations of electrode–absorber heterostructures include Pt/MAPbCl₃/Ti/Au⁴⁷ and Au/MAPbI₃ PDs⁴⁵, which display lower $R \sim 0.0469$ and 0.10 A/W, respectively, while the Pt/MAPbCl₃/Ti/Au⁴⁶ and Au/MAPbI₃⁴⁷ showed $10^3 \times$ lower values of D compared to the Ag-perovskite PD demonstrated here.

Figure 4b displays the EQE obtained for both PDs as a function of T at $F \sim 5.24$ $\mu\text{W}/\text{cm}^2$ (0.00524 mW/cm²). 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:

$$\text{EQE} = R \frac{hc}{\lambda q} \quad (7)$$

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 ~ 300 K for the Gr-perovskite and Ag-perovskite, respectively. High EQE values have previously been reported^{48–50} for WSe₂, graphene/Si, and GeS-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 result⁵⁰. The inset in Fig. 4b shows the EQE as a function of F , where the EQE decreases with increasing F . At $F \sim 5.24$ $\mu\text{W}/\text{cm}^2$ (~ 0.00524 mW/cm²), the EQE $\sim 103\%$, whereas at $F \sim 10.75$ mW/cm², 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

Fig. 4 Device figures of merit for the 2D perovskite PD. **a** R as a function of F , where the highest R was found to be ~ 0.27 and 0.53 A/W at $F \sim 5.24 \mu\text{W}/\text{cm}^2$ ($0.00524 \text{ mW}/\text{cm}^2$) for Gr-perovskite and Ag-perovskite PDs, respectively. The inset shows D as a function of F , where D was calculated to be $\sim 1.55 \times 10^{13}$ Jones and 3.24×10^{13} Jones for Gr-perovskite and Ag-perovskite, respectively. **b** The EQE as a function of T (~ 4 – 350 K). The EQE increases considerably with increasing T , and at room temperature, EQE was determined to be $\sim 78\%$ and 103% for the Gr-perovskite and Ag-perovskite PDs, respectively. The inset shows the EQE as a function of F for both PDs. **c** ON/OFF ratio comparison for both PDs at $T \sim 4$ – 350 K. At ~ 300 K, the ON/OFF ratios were $\sim 2 \times 10^3$ and 3.4×10^3 for Gr-perovskite and Ag-perovskite PDs, respectively. **d** The I_p as a function of λ for the Gr-perovskite PD, while the inset shows the corresponding I_p versus λ for the Ag-Perovskite PD at $T \sim 200$, 300 , and 350 K.

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 $T \sim 4$ – 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 3.4×10^3 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 ~ 30 X higher compared to prior PD reports based on other perovskites, such as $\text{CH}_3\text{NH}_3\text{PbI}_3$ ^{6,47} and CsPbBr_3 ⁵¹, where the ON/OFF ratios reported were $\sim 10^2$. In yet other similar studies, where polycrystalline $\alpha\text{-FAPbI}_3$ 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 λ was varied from 400 to 2300 nm. The filters were switched between the measurements due to the restriction in ranges

(400 – 1000 nm, Filter- M000010357; 1000 – 2300 nm, Filter-M000010266). Figure 4d exhibits the I_p versus λ plot for the Gr-perovskite PD at $T \sim 200$, 300 , and 350 K, while the inset shows the corresponding I_p versus λ for the Ag-perovskite PD, where the measurements were made in vacuum at a bias of 40 V. In both cases, the maximum I_p was found at $\lambda \sim 630$ nm, which is consistent with the bandgap $E_g \sim 1.96$ eV for our 2D perovskite material. The E_g value obtained closely matches the data from prior reports on 2D $(\text{BA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13}$, where $E_g \sim 1.91$ eV was reported²¹, which suggests that the photons with energy < 1.96 eV will not cause optical excitation and thus there is little absorption within the PD devices. Although our synthesized 2D perovskite showed absorption arising over a relatively broad range from $\lambda \sim 400$ to 880 nm, the I_p was least for $\lambda > 850$ nm, given the maximal λ range measured was 2300 nm. Apart from the photon energy of 1.96 eV, this I_p reduction may also be due to defects and trap states within the layers, which annihilate the generated electron-hole pairs due to non-radiative decay mechanisms.

Figure 5a, b displays the temporal response of I_p to ON/OFF optical radiation pulses at $T \sim 100$, 200 , 300 , and 350 K with $F \sim 10.75 \text{ mW}/\text{cm}^2$ for the Gr-perovskite and Ag-perovskite PDs, respectively, where the “ON” pulses are shaded in the first two cycles, as examples. The ON/OFF cycling measurements were conducted using a semiconductor parameter analyzer B1500A and

Fig. 5 Temperature-dependent temporal response. Temporal response of I_p to periodic broadband light pulses, represented by shaded regions as examples for the first two switching cycles, where I_p is plotted for $T \sim 100, 200, 300$, and 350 K at $F \sim 10.75$ mW/cm² for **a** Gr-perovskite and **b** Ag-perovskite PDs. The τ_{rise} and τ_{fall} as a function of T , where the $\tau_{rise} \sim 31$ ms and $\tau_{fall} \sim 27$ ms were measured for **c** Gr-perovskite PD, while for **d** Ag-perovskite PD, the $\tau_{rise} \sim 17$ ms and $\tau_{fall} \sim 45$ ms at 300 K. At $T \sim 4$ K, the τ_{rise} and τ_{fall} values were found to be ~ 59 and 28 ms, respectively, for Ag-perovskite PD.

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 slower⁵³. 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 , where the Ag-perovskite PD demonstrated higher I_p compared to the Gr-perovskite PD biased at 40 V over the entire temperature range tested. Figure 5c, d shows a more in-depth analysis of the rise and decay time measurements obtained from our devices. The rise time τ_{rise} and fall time τ_{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 , respectively⁵⁴. At ~ 300 K, $\tau_{rise} \sim 31$ ms and $\tau_{fall} \sim 27$ ms were determined for the Gr-perovskite PD, while $\tau_{rise} \sim 17$ ms and $\tau_{fall} \sim 45$ 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 $\text{CH}_3\text{NH}_3\text{PbI}_3$ PD devices⁴⁷. Table 1 summarizes the τ_{rise} and τ_{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 carriers⁵⁵. For both PDs, the τ_{rise} and τ_{fall} seem to decrease nonlinearly with increasing T , although the τ_{fall} for the Ag-perovskite PD at ~ 300 K seems to increase compared to the τ_{rise} , which suggests that recombination of the photocarriers occurs over a longer duration at room T for the Ag-perovskite. Generally, the values of τ_{rise} and τ_{fall} were lowest for $T \sim 100$ 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 previously³⁹. 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

Fig. 6 Strain dependency. **a** Five repetitive cycles of the I_p versus F , when the Ag-perovskite PD was on a flat surface. The I_p did not change significantly for all the five cycles tested over the entire range of F tested, which confirms the reproducibility of our inkjet-printed PD devices. **b** Schematic diagram of the strained Ag-perovskite PDs, while under illumination which was inkjet printed on the flexible PI substrate. **c** The change in I_p as a function of F for various strain/curvature levels: ~ 0.072 , 0.087 , 0.112 , 0.157 , and 0.262 cm⁻¹. **d** The dependency of I_p as a function of curvature for various F , where the I_p decreased as the curvature increased.

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 μ W/cm² up to the maximum of 32 mW/cm² with a time delay of 5 s in between each incremental F to stabilize the response. The F was then lowered from ~ 32 mW/cm² back down to ~ 58 μ W/cm², 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 $F \sim 58$ μ W/cm² 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 $\sim 57\%$, 26% , 21% , 16% , and 12% for $F \sim 1.2$, 8.2 , 18.9 , 26.8 , and 32 mW/cm², 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 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 hetero-junction 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 CH₃NH₃⁺ molecules, and these strain-induced structural variations in the crystalline order result in reduced photocarrier generation. Their studies⁵⁶ also shed insights on the photovoltaic properties of CH₃NH₃PbI₃ under external strain, where the absorption efficiency of incoming photons was lower.

In summary, we have synthesized (CH₃(CH₂)₃NH₃)₂(CH₃NH₃)_{n-1}Pb_nI_{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 Φ_B 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 $R \sim 0.53$ 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, τ_{rise} and τ_{fall} for the Ag-perovskite PD were at least 30 X and 8 X higher, respectively, compared to prior reports. The λ -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 $(\text{CH}_3(\text{CH}_2)_3\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_3\text{Pb}_4\text{I}_{13}$ perovskites, which is a family of layered compounds with tunable semiconducting properties. The PbO (part #: 402982), HI (part #: 210021), H_3PO_2 (part #: 214906), $\text{CH}_3\text{NH}_3\text{Cl}$ (part #: 8060200250), and $n\text{-CH}_3(\text{CH}_2)_3\text{NH}_2$ (part #: 471305) were purchased from Sigma-Aldrich. The PbO powder (2232 mg) was dissolved in a mixture of 57% w/w aqueous HI solution (10.0 mL) and 50% aqueous H_3PO_2 (1.7 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 $\text{CH}_3\text{NH}_3\text{I}$ (507 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 $n\text{-CH}_3(\text{CH}_2)_3\text{NH}_3\text{I}$ (248 μL) and hydriodic acid (5 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 pressure²¹.

2D perovskite ink formulation

Perovskite inks were formed using a magnetically stirred solvent engineering process. The 30 mg/mL of $(\text{CH}_3(\text{CH}_2)_3\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_3\text{Pb}_4\text{I}_{13}$ powder was dissolved in 10 mL of DMF and magnetically stirred overnight at 500 rpm at room T , as shown in Fig. 1a—left. Then the solution was kept at room T for 30 min to stabilize the solution for inkjet printing. The solubility of the perovskite precursor in DMF is excellent, as DMF is less volatile and hygroscopic in nature compared to other typical solvents used in inkjet printing, such as N -methylpyrrolidone. Using DMF as the solvent for perovskite inks has previously been reported⁵⁷, which guided us to adopt this for our ink formulations. The top 3 mL of the perovskite ink was then transferred to the cartridge of the Dimatix Materials Printer (DMP-2850 Series) for our subsequent device fabrication efforts using inkjet printing.

Gr and Ag ink formulations

Both Gr (SKU # 496596) and Ag (SKU # 327085) powders were purchased from Sigma-Aldrich, which had a purity of $\geq 99.99\%$ for trace metals, while the particle size was ~ 45 and $2\text{--}3.5\ \mu\text{m}$ as received, for the two materials, respectively. Additionally, the liquid exfoliated Gr ink was characterized using Raman spectroscopy where three distinct Raman peaks were observed at $1361\ \text{cm}^{-1}$ (D -band), at $1580\ \text{cm}^{-1}$ (G -band), and at $2713\ \text{cm}^{-1}$ ($2D$ -band). The D -band indicates the defective structure of exfoliated graphite sheets, while the G - and $2D$ -bands indicate the order and purity of the characteristic graphite/graphene sheets, respectively⁵⁸. Raman Spectroscopy has previously been used to tabulate the I_D/I_G and I_{2D}/I_G ratios, where the latter is correlated to thickness. For example, Nguyen et al.⁵⁸ notes that when the ratio $I_{2D}/I_G \sim 2\text{--}3$, it is reflective of monolayer graphene, when $2 > I_{2D}/I_G > 1$, bilayer graphene results, and finally for multilayer graphene, the $I_{2D}/I_G < 1$. Our liquid exfoliated graphene showed ratios for $I_D/I_G \sim 0.04$ and $I_{2D}/I_G \sim 0.28$, where the latter clearly indicates that our liquid exfoliated graphene is multilayer⁵⁸. The conducting inks for the electrodes were produced through ultrasonic bath sonication of Gr or Ag powder in 2-propanol (IPA) as shown in Fig. 1a—right. An initial concentration of ethyl cellulose of $\sim 0.8\ \text{wt}\%$ and 50 mg/mL of Gr or Ag powder was then added, respectively, in 10 mL of IPA and placed in a Branson Bath Sonicor (CPX2800) for 24 h. The top 8 mL of the supernatant was removed and placed in a new vial, which was later transferred to the cartridge of the inkjet printer. The formulation of the Gr or Ag with IPA is challenging compared to the other inks, such as MoS_2 ink with Cyclohexanone/Terpeneol solvent⁵⁹, because the IPA-based inks

frequently clog the nozzles; the IPA solvent dries out fast and makes the Gr/Ag platelets to compromise the performance of the nozzle head, so frequent nozzle cleaning is necessary, as reflected in Fig. 1b. For nozzle cleaning, the cartridge head was placed in a small glass beaker filled with IPA, which was then sonicated for 2 min to remove the nozzle clogs.

Inkjet-printed heterostructure PD fabrication

A $2 \times 1.5\ \text{mm}$ perovskite layer was first printed with 30 ink passes on a flexible PI substrate. Printing the perovskite ink is challenging compared to other 2D printed materials such as MoS_2 or graphene inks^{59,60}. Solubility is one issue even after the printed layer becomes solid, since the subsequent layer can dissolve the initial layer, as the addition of the newly printed ink makes it soluble again. That is why a stable base layer is required so that the other printed layers can stay confined within the printed area. To make a stable base layer, four nozzles were used to print five passes and allowed to stabilize for 15 min to alleviate the surface tension between the printed ink and the flexible PI substrate. Then, the rest of the 25 passes were printed. The printing parameters, such as drop spacing, were kept at $30\ \mu\text{m}$, platen $T \sim 40^\circ\text{C}$, the jetting voltage $\sim 21\ \text{V}$, and these parameters have been optimized after many iterations. The printed perovskite was annealed at 30°C for 30 min on a hot plate, where the T was ramped to 100°C (T ramp rate $\sim 30^\circ\text{C}/\text{min}$) and, subsequently, the film was annealed for 30 min. Thermal annealing is a crucial step to accelerate the reaction between the organic and inorganic species in the perovskite compound. Dualeh et al.⁶¹ established that densely interconnected films are obtained by annealing the perovskite at 80°C for 3 h, or 100°C for 45 min, respectively. When the T is lower than 80°C , the perovskite phase formation appeared to be hindered. Furthermore, prolonging the annealing time at low- T does not provide any advantage for film quality. On the other hand, the perovskite films annealed at T more than 100°C will produce secondary phases of PbI_2 , likely originating from the decomposition of MAPbI_3 ⁶¹. Using excessively high or low processing T will thus cause undesired film quality, as a result of slow reaction rates or additional side/decomposition reactions.

After annealing the perovskite layer, the PI substrate was placed back onto the platen at the same (x,y) coordinates for printing the Gr/Ag contacts, where ~ 25 ink passes were used, and the films were annealed at 100°C for 30 min. The separation between the metal electrodes was $\sim 800\ \mu\text{m}$ and the width of each electrode was $\sim 600\ \mu\text{m}$, as the contact layers were printed on top of the perovskite layer.

DATA AVAILABILITY

The data that support the findings of this study are available upon the request from the corresponding author.

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AUTHOR CONTRIBUTIONS

A.B.K. conceived the overall project. R.F.H. conducted the experiments related to ink formulation, inkjet printing, material characterization, and device measurements. M.M. developed techniques to synthesize the 2D perovskites. L.-C.M. and S.R.S. contributed to discussions related to figure edits. A.B.K. and R.F.H. analyzed the data, conducted significant paper edits, and came up with the conclusions. All reviewed the paper writing and approved of its content.

COMPETING INTERESTS

The authors declare no competing interests.

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