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High responsivity and response speed single-layer mixed-cation lead mixed-halide perovskite photodetectors based on nanogap electrodes manufactured on large-area rigid and flexible substrates

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Abstract

We employ mixed-cation lead mixed-halide perovskites as the photoactive material in single-layer solution-processed photodetectors fabricated with coplanar asymmetric nanogap Al-Au and indium tin oxide (ITO)-Al electrodes. The nanogap electrodes, bearing an interelectrode distance of ≈ 10 nm, are patterned *via* adhesion lithography, a simple, low-cost and high-throughput technique. Different electrode shapes and sizes are demonstrated on glass and flexible plastic substrates, effectively engineering the device architecture, and, along with perovskite film and material optimisation, paving the way towards devices with tunable operational characteristics. The optimised coplanar nanogap junction perovskite photodetectors show responsivities up to 33 A W^{-1} , specific detectivity in the order of 10^{11} Jones, and response times below 260 ns, whilst retaining a low dark current (0.3 nA) under -2 V reverse bias. These values outperform the vast majority of perovskite photodetectors reported so far, while avoiding the complicated fabrication steps involved in conventional multi-layer device structures. The work highlights the promising potential of the proposed asymmetric nanogap electrode architecture for application in the field of flexible optoelectronics.

1. Introduction

Photodetectors are ubiquitous electronic devices that convert optical signals to electrical and can be found in multiple applications ranging from imaging to communication and remote sensing.^[1-3] Recent progress within the wider field of flexible and printed electronics has paved the way for flexible photodetectors to be implemented in wearable, biomedical, and low-power optoelectronic devices.^[4, 5] This is also driven by the developments in novel functional materials, which combine exceptional electrical and optoelectronic properties, as well as outstanding mechanical flexibility, while they can be processed from solution at low-temperature using inexpensive fabrication methods.^[6]

Hybrid organic-inorganic metal halide perovskite materials, comprising the general structure ABX_3 , where the A site at its centre is an organic or inorganic cation (e.g. $CH_3NH_3^+$, $CH_3NH_2NH_2^+$, Cs^+), B is a metal cation (usually Pb or Sn), and X is an halide anion (Cl^- , Br^- , or I^-), have emerged as outstanding light harvesting materials.^[7] Their intriguing set of characteristics, such as long charge-carrier diffusion length,^[8] ambipolar charge transport,^[9] broadband absorption and solution processability, has supported their meteoric rise, primarily within the photovoltaics community.^[10, 11] The application of metal halide perovskites as active materials in low-cost solar cells prompted dramatic increase in their efficiency above 20%, unveiling their great potential for commercial exploitation.^[12] Notwithstanding the exceptional solar cell performance obtained, another attractive attribute is the fact that they can be used in conjunction with flexible substrates enabling thus the development of portable and wearable optoelectronic devices.^[13] For this reason, perovskites have also been recently explored in other optoelectronic applications,^[14, 15] such as photodetectors,^[16, 17] light-emitting diodes,^[18] field-effect transistors^[19, 20] and resistive switching memory devices,^[21] while some of these devices have already been demonstrated with flexible (plastic) substrates.^[22] More specifically, with regard to perovskite-based photodetectors, outstanding performance has been obtained with photodiodes, photoconductors and phototransistors, showing responsivities up to 10^4 A W^{-1} ,^[23]

detectivity values exceeding by far those of standard Si photodiodes (10^{12} - 10^{14} Jones)^[24, 25] and fast photoresponse below nanoseconds.^[26] However, the most efficient device structures commonly comprise multiple layers, many manufacturing steps and/or time and power consuming techniques. Therefore, there is a need for simplifying the device architecture, while employing manufacturing processes compatible with inexpensive large-area printed electronics industries, without sacrificing dramatically the performance characteristics.

The most commonly used device architecture is the vertical (sandwich-type) one, where several layers bearing different functionalities are stacked sequentially on top of each other, while at least one of the electrodes needs to be transparent with an Indium Tin Oxide (ITO) coated glass substrate being commonly used. On the other hand, lateral (coplanar) architectures are usually employed along with materials of lower dimensionality, such as nanosheets and nanowires, which tend to suffer from discontinuous surface coverage, or small particles exhibiting poor wettability; all these materials would lead to significant leakage current in vertical devices.^[7] The lateral design presents certain advantages over the vertical one, namely no particular requirement for transparent conductive contacts, ease of fabrication and facile integration with the backplane thin film transistor (TFT) imager circuit.^[27] Furthermore, photodetectors bearing the much simpler (single-layer) architecture, may be advantageous not only from a fabrication standpoint but also in terms of performance. For instance, to obtain high response speed, the inter-electrode distance must be reduced and to achieve this, ultra-thin films are required. The latter presents specific challenges when it comes to the formation of high quality ultra-thin (<50 nm) films, while such films inevitably result in reduced absorption and thus lower photocurrent. Hence, usually the responsivity requirements have to be compromised over fast photoresponse. By using nanogap-separated coplanar asymmetric electrodes, the effect of this trade-off may be minimised. However, the scalable fabrication of such electrodes is not always trivial.

Herein we employ an innovative, simple, low-cost nanopatterning technique, named adhesion lithography (a-Lith),^[28] for the fabrication of nanogap coplanar electrodes, eliminating thus the need for expensive equipment as well as complicated process steps involved in alternative techniques.^[29] Similar nanogap electrode architectures have already been used to develop high frequency diodes,^[30-32] resistive memories,^[33] nanoscale polymer light-emitting diodes^[34] and field-effect transistors^[35-37] on a variety of substrate materials. In this work we combined asymmetric nanogap electrodes composed of either aluminium-gold (Al-Au) or Al-indium tin oxide (ITO), with the solution processable metal halide perovskite $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}[\text{I}_{0.9}\text{Br}_{0.1}]_3$ ^[38] (termed FACs, where FA is formamidinium), to produce planar photodetectors featuring interelectrode nanogaps of ≈ 10 nm with widths in the range of 4 to 50 nm. Importantly, the low process temperature requirements of a-Lith allows devices to be fabricated on both glass as well as flexible poly(ethylene terephthalate) (PET) substrates without adversely affecting their operating characteristics. Optimised planar photodetectors exhibit state-of-the-art performance characteristics with responsivity and specific detectivity values of 33 A W^{-1} and 10^{11} Jones, respectively, and response times of 260 ns.

2. Results and Discussion

2.1. Electrode Patterning and Material Characterisation

Square-shaped coplanar Al-Au asymmetric electrodes with total electrode width and interelectrode (nanogap) distance of 4 nm and ≈ 10 nm, respectively, (**Figure 1a-b**) were patterned *via* a-Lith following previously reported procedures.^[28, 35] The method is simple, versatile and high throughput, able to deliver devices of arbitrary shape on a variety of substrate materials. The mixed-cation lead mixed-halide perovskite with chemical structure $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}[\text{I}_{0.9}\text{Br}_{0.1}]_3$ is one of the best performing photoactive materials of the hybrid metal halide perovskite family and was selected owing to its excellent optical and transport properties as well as due to its improved environmental stability.^[38] To fabricate the photodetecting

devices, a FACs precursor solution was spin-coated on top of the a-Lith patterned electrodes, covering both the nanogap area and the electrodes' surface. A side view of the coplanar nanogap device structure is depicted in **Figure 1c**. We note here that our coplanar device architecture is by default advantageous to the conventional sandwich structures, in the sense that the metals (in this instance Al and Au) are not thermally evaporated on top of the metal halide perovskite, reducing thus the probability for a detrimental chemical reaction to occur at the interface.^[39] In fact, the native AlO_x layer formed on the surface of Al electrode before perovskite deposition, may serve as protective layer at the Al/perovskite interface, something effectively valid in mesoscopic perovskite photovoltaics.^[40] A way to completely circumvent this issue at a later stage would be to replace reactive metals, such as Al, for instance, with Cu, an inexpensive metal that has been reported lately to enhance the stability of perovskite solar cells^[41] or to employ suitable surface barriers^[42] and surface passivation techniques^[39].

From the optical absorption spectrum (**Figure 1d**), it can be seen that the FACs perovskite has a broadband absorbance, covering the whole visible range up to ≈ 800 nm. The emission spectra of the three light-emitting diodes (LEDs) used to excite the nanogap photodetectors are overlapping with the FACs absorption spectrum. **Figure 1e** depicts the alignment of the perovskite's energy levels with the work function of the Al and Au electrodes in a flat band configuration and it shows that the barrier for charge injection/extraction is similar for both electrons and holes (0.4 and 0.5 eV at the Al and Au interfaces, respectively), while larger Schottky barriers form at the opposite contacts (≈ 1.1 eV for electrons at perovskite/Au interface, and ≈ 1.2 eV for holes at the perovskite/Al contact). However, the band bending and barrier thinning that occur upon biasing the device in the dark, induce a small current rectification owing to the asymmetric contacts (**Figure S1**). On the other hand, under illumination the resulting built-in field facilitates the separation of weakly bound photogenerated electron-hole pairs^[43, 44] giving rise to a photocurrent, which is further increased due to the injected carriers

when an (electro)negative voltage ($V < V_{bi}$) is applied (**Figure 1f**), highlighting thus the suitability of these planar nanogap devices for photodetector applications.

The impact of FACs molar concentration on film formation atop the nanogap electrodes was studied in order to identify the best suited conditions for reliable fabrication of devices with optimised performance. **Figure 2a-d** shows the atomic force microscopy (AFM) images of FACs films deposited from solutions with increasing concentrations from 0.25 to 2 M. We find that increasing the concentration of the precursor solution alone, results in not only different film thicknesses but also affects the layer morphology. All films depict a granular topography with grains growing in size as the concentration increases. It is noteworthy that the film spin-cast from the less concentrated solution (0.25 M) shows a bimodal height distribution, owing to the larger grains (60-100 nm height) not fully covering the top surface layer, while the underlying layer consists of much smaller grains. For concentrations >0.5 M (**Figure b-d**), the top layer is fully covered with the larger grains having a peak-to-valley height $\Delta z = 60-80$ nm and monomodal height distribution (**Figure 2e**). The perovskite grains are substantially larger in the thickest film, derived from the highest concentration solution (2 M, **Figure 2d**), with diameters around 300 nm, as compared for instance with the thinner 1 M concentration film where the vast majority of grains have a diameter <200 nm. The grain size is directly related to the grain boundaries present in the film, which are known to act as scattering centres, lowering the charge carrier mobility and decreasing the excitons diffusion length.^[45, 46] Therefore, the bulk film morphology is anticipated to play a key role in the photodetector performance as well.

The difference in surface film morphology upon increasing the precursor solution concentration is also depicted in the optical microscopy images shown in **Figure 2f-g**. More specifically, **Figure 2f** shows the 0.5 M perovskite film topography on top of the two metals using a $50\times$ magnification in bright field mode, while **Figure 2g** is a lower magnification ($5\times$) image, recorded in dark field mode to enhance the contrast; it reveals the boundaries of Al and Au electrodes that are covered by the film formed using the highest molarity precursor solution

(2 M). Despite the lower magnification, large interconnected wrinkles can be discerned on the surface of the thickest film, having a thickness of around 500 nm as estimated from cross-section scanning electron microscopy (SEM) (**Figure 2h**), in contrast to the much smoother topography of the thinnest (0.25 M) film (**Figure S2**). The nanogap channel length in all cases was <20 nm, as depicted in the cross-sectional SEM and TEM images (**Figure S3**), in accordance with previously published data.^[28, 31, 35]

2.2. Device Characterisation

The most important figures-of-merit of a photodetector are the responsivity (R), specific detectivity (D^*) and response time (τ). Depending on the application, a broadband or narrowband photoresponse at certain wavelengths may be sought after. The herein fabricated coplanar nanogap photodetectors are responsive to all visible wavelengths and, as such, to red ($\lambda_{\text{max}} = 632 \text{ nm}$), green ($\lambda_{\text{max}} = 525 \text{ nm}$), blue ($\lambda_{\text{max}} = 475 \text{ nm}$) (RGB) LEDs, when illuminated under the same light intensity (**Figure S1**). For simplicity, we focus our study on green ($\lambda_{\text{max}} = 525 \text{ nm}$) excitation wavelength, although we note that similar results were obtained also under red and blue illumination wavelength.

2.2.1. Steady-State Electrical Characterisation

Figure 3a shows the semilogarithmic I - V curves of devices fabricated from precursor solutions with increasing concentration (0.25 to 2 M) in dark and under illumination with the green ($\lambda_{\text{max}} = 525 \text{ nm}$) LED at a light intensity of 1.67 mW cm^{-2} . All devices exhibited high resistance in the dark, with currents as low as 0.3-0.6 nA, and no (or little) rectification was observed in the voltage range -2 to 2 V owing to the large barriers present at the perovskite/metal interfaces. This is in contrast to other reports of phototransistor devices employing asymmetric Al-Au source-drain contacts separated with 30 nm gap fabricated *via* angle evaporation technique,^[47]

where significant leakage current was present in the dark. This attribute highlights the excellent electrical isolation obtained in the a-Lith fabricated nanogap electrodes. However, when illuminated, the current increased in both positive and negative bias, albeit with a very low rectification ratio ($I_{reverse}/I_{forward} \approx 1.3$), reminiscent of a photoconductor. This implies that the previously existing Schottky barriers at the electrode/perovskite interfaces have changed into ohmic under illumination, facilitating charge injection and extraction even when a small bias is applied. Furthermore, it is noteworthy that the open circuit voltage (V_{OC}) of the 2 M device is significantly shifted to lower voltages as compared to devices made from the lower molarity formulations. We shall note here that the voltage where current is minimum in the dark (related to the V_{bi}) lies >2 V. Therefore, the V_{OC} shift is actually *larger* in the higher concentration case. A simple explanation could be given if we take into account the different film morphology of each film, as presented in Fig. 2, which may be correlated with the amount of trap states that are expected to exist in the different films, and this, in turn, would give rise to different recombination rates and subsequently V_{OC} values.^[48] Based on this rationale and our experimental results, we can infer that the smaller grain size in the films obtained with the lower concentration precursor solutions would have more surface traps than the larger crystallite size films obtained from higher molarity solutions, hence the larger V_{OC} shift (from dark state). A more detailed analysis elucidating the origin of the V_{OC} shift, aided by device simulations is currently under way, as it becomes clear that properly engineering the material and the device to deliver a certain V_{OC} value is essential to achieve (low) voltage operation of the herein proposed photodetectors.

The device responsivity (R) was calculated at ± 2 V by considering the geometrical area of the nanogap as the active area of the photodetector. Generally, the responsivity is defined as the ratio of photogenerated current to the optical power of the light incident to the detector at a certain wavelength (**Equation 1**):

$$R = \frac{I_{ILL} - I_D}{P \cdot A_{ILL}} \quad (1)$$

where I_{ILL} is the measured current under illumination, I_D is the current in the dark, P is the power density of the LED used and A_{ILL} the photodetector geometrical area illuminated by the LED. The latter is defined here as the product of the electrode width (corresponding to the perimeter of the square Al electrode; $w = 4$ mm) and the ≈ 10 nm gap separating the asymmetric electrodes. It can be observed that the current increases as the concentration of the precursor solution increases, reaching ≈ 12 nA – about 30 times higher with regard to the dark current – for the highest concentration of 2 M. This is also reflected in the responsivity calculated in reverse (-2 V) and forward (+2 V) bias as a function of solution concentration, which shows a slow linear increase in the responsivity for lower concentrations (0.25-1 M) and an abrupt increase for the 2 M with highest value $R = 33.7 \text{ A W}^{-1}$ (**Figure 3b**). The results are in agreement with the film morphology analysis (*vide supra*), where the 2 M solution resulted in films with bigger grains, less grain boundaries and large interconnected domains (higher coverage), all associated with better charge transport. From **Figure 3a** and **3b** it is also deduced that the photodetector in principle can be operated under both positive and negative bias, but since the responsivities are slightly higher at negative bias, we conclude that this is the optimum operation condition. We shall note here that our devices presented significant hysteresis under linear double voltage sweeps in forward and reverse direction (**Figure S4**); a phenomenon initially observed and well-studied in perovskite-based photovoltaic cells without suitable interfacial/passivation layers^[49]. However, we would like to note that this phenomenon is not directly relevant to the photodetector operation, as in this case we operate the device at a certain voltage instead of performing linear sweeps. More importantly, as the nanogap perovskite photodetectors photoresponse lies in the hundreds of nanoseconds range (*vide infra*), which is orders of magnitude faster than the ions movement, which is mainly responsible for the observed hysteresis, it is believed that this effect does not affect the photodetector operation.

Given that the devices were illuminated from the bottom side (through the transparent glass substrate, see **Figure 1c**), the photoinduced carriers that are generated in this area, transit the short nanochannel and finally are collected at the electrodes. However, given a penetration depth of $\delta = 330$ nm at 525 nm, as calculated from the absorbance spectrum shown in **Figure 1d** for a perovskite film thickness of $t = 500$ nm ($\delta = 1/\alpha$, where $\alpha = 3 \times 10^4$ cm⁻¹ is the absorption coefficient of the FACs layer), we cannot rule out that electron-hole pairs are photogenerated in a larger volume than that enclosed by the nanogap area (40 μm^2) and the metal thickness (40 nm). Therefore, we may rationalise the high photocurrent and responsivity obtained for such nanostructures by taking into account the above considerations along with the high charge carrier diffusion length of this mixed-cation lead mixed-halide perovskite that can reach values of 2.9 μm .^[38, 46]

The external quantum efficiency (*EQE*) of the device was also calculated from the responsivity at $\lambda = 525$ nm via **Equation 2**:

$$EQE = \frac{hc}{q\lambda} R(\lambda) = \frac{1240}{\lambda[\text{nm}]} R(\lambda) \quad (2)$$

where h is Planck's constant and c the speed of light. An *EQE* = 7960% for the 2 M device was calculated. As expected, the *EQE* is higher than 100%, implying a photoconducting gain of $\gg 1$. When the device is biased at -2 V, injected carriers add up to the photogenerated ones, which are effectively separated and transferred to the respective electrodes, driven by both the internal built-in electric field and the externally applied negative voltage, and contribute to the measured current and external efficiency (see schematic depicting the operational principle under illumination and application of a negative voltage in **Figure 1f**).

Next, we studied the effect of incident light intensity on the 2 M device. **Figure 3c** depicts the *I-V* characteristics upon increasing light intensity of the green-emitting LED from 45 to 890 $\mu\text{W cm}^{-2}$. The logarithmic plot of photocurrent as a function of light intensity was fitted to a power law equation ($y = bx^a$) from which $a=1.1$ was obtained (**Figure 3d**). This

corroborates a highly efficient device in which all excited electrons/holes are captured by electrodes prior to recombination.^[50] Furthermore, no saturation of the photocurrent is observed in the light intensity range tested, as evidenced also by the linear increase of photosensitivity ($S = I_{ILL}/I_D$) with light intensity (**Figure S5**). This linear dependence is attributed to the linear photogeneration of electron-hole pairs at reverse bias ($I_{ILL} = qGL$, where q is the elemental charge, G is the photogeneration rate and L is the interelectrode spacing)^[51] in accordance with balanced electron-hole mobilities expected in the FACs film.^[9] The small V_{oc} change under increasing illumination intensity can be rationalised by taking into account their logarithmic ($\ln$) dependence, although more detailed study of the origin of the V_{oc} shift is currently underway.^[48]

By taking advantage of the versatility offered by a-Lith technique in fabricating electrodes with varying shapes and sizes, we patterned interdigitated Al-Au electrodes with increasing electrode widths (w) on glass substrates. Electrodes with w of 1, 2 and 5 μm were fabricated, while the interelectrode distance remained in the range 10-15 nm. An optical micrograph of the bare electrodes accompanied with an SEM image of the surface topography of the completed device are shown in **Figure 4a**. The electrical characteristics of the nanogap photodetectors upon scaling the electrodes width are shown in **Figure 4b**. The current scales with the coplanar nanogap electrode width in accordance with previous reports of deep UV photodetectors^[52] and polymer light-emitting devices^[34] fabricated *via* a-Lith. Interestingly, the photocurrent increases with a higher rate than the dark current, as revealed by the slope of the linear fittings of the dark and photocurrent *vs* diode width plot depicted in **Figure 4c**. This results in higher overall photosensitivity for the longer electrode widths, presenting thus an efficient strategy to improve the performance of the nanopatterned coplanar photodetectors. The versatility in patterning different electrode geometries presented by a-Lith enables this optimisation without compromising the interelectrode channel length. Upon plotting the photosensitivity as a function of applied voltage for the varying width devices (**Figure 4d**), the

optimum operation voltage can also be extracted. The photosensitivity is highest under positive bias of 1 to 1.5 V. We attribute this to the large built-in potential at the Al/FACs/Au device measured in the dark. Since the dark current at this voltage reaches its lowest value, the device photosensitivity maximises.

Furthermore, scaling of the diode's width may also be employed to improve the detectivity of the coplanar photodetectors, as shown in **Figure 4e**. Specific detectivity (D^*) is a measure of the photodetector ability to discern low intensity signals from the noise current normalised to the active area of the device and electrical bandwidth of the noise measurement. The accurate determination of specific detectivity must take into account all potential types of noise, i.e. thermal, shot, flicker and generation-recombination noise, especially when disordered semiconducting materials are involved.^[16, 53] Here we use the simplified **Equation 3** for the calculation of D^* with the sole purpose to showcase the effect of scaling the electrode width on detectivity:

$$D^* = \frac{\sqrt{A_{ILL}R}}{\sqrt{2eI_D}} \quad (3)$$

D^* values in the order of 10^{11} Jones were obtained, which increased as a function of the device area (**Figure 4b**), since the dark current remained sufficiently low (<1 nA at -2V), as compared with other perovskite photodetector devices of similar architecture (for instance dark current values of 0.6-0.8 nA at 5-6 V have been reported for coplanar nanosheet 2D CsPbBr₃ photodetectors).^[13, 54]

2.2.2. Time-Dependent Photoresponse

The speed of the photodetector is a very important figure of merit, especially for applications demanding fast photoresponse, such as optical communications, smart imaging and spectroscopy.^[55, 56] The photodetector response time (τ) is defined as the time needed for the output (electrical) signal to reach (or decay to) $(1-e^{-1}) = 63\%$ of its peak value upon an incident

optical signal.^[57] Several techniques are employed to measure τ . A straightforward way is by determining the -3dB frequency (f_{-3dB}) or cut-off frequency of the device, namely its bandwidth, upon recording the photocurrent signal attenuation until 70.7% of its initial value (I_0) as the modulation frequency of the input signal increases. This frequency is related to the response time through **Equation 4**:

$$f_{-3dB} = \frac{1}{2\pi\tau} \quad (4)$$

Another widely used measurable quantity is the rise and fall time (t_r and t_f , respectively) corresponding to the time it takes to the photocurrent to rise (fall) from 10% (90%) to 90% (10%) of its peak value upon illumination with a modulated optical pulse.^[57] The empirical formula correlating the cut-off frequency with the rise (fall) times is given as:

$$f_{-3dB} = \frac{0.35}{t_r} \quad (5)$$

Combining Eqns. (4) and (5) yields another relationship linking t_r (or t_f) and τ :

$$t_r = 2.2\tau \quad (6)$$

However, the response speed of an actual photodetector device may be limited by one or more of the following time components; (a) the RC time constant of the equivalent circuit, namely the resistance R (due to series and contact resistance components) and the capacitance C (device junction capacitance) and of the measurement system (load resistance, parasitic capacitances), (b) the drift time constant, defined as the charge carriers transit time (t_{tr}):

$$t_{tr} = \frac{d^2}{\mu V} \quad (7)$$

where d is the interelectrode distance, μ the semiconductor mobility and V the applied (if any) and the built-in voltage, and (c) a diffusion time component, usually in the case when the junction is not fully depleted. We expect our nanogap devices to be limited mainly by the RC time constant, as the drift component should be much faster (<ps) given the FACs' high carrier mobility ($21 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)^[38] and the tiny nanogap length (10 nm), while diffusion time should not contribute to the time response as the nanogap junction is fully depleted.

Given the different definitions mentioned above and to remove any ambiguity in the evaluation of the nanogap photodetector speed, we applied three different measurement protocols and discuss the results obtained in each case with respect to the limitations of the respective experimental setup. First, we explored the dynamic behaviour of our devices by measuring the photoresponse of the 2 cm long nanogap perovskite photodetector at a bias $V = -1$ V upon modulating the green LED source with frequencies 1 Hz to 1 kHz at a light intensity of 0.9 mW cm^{-2} , as shown in **Figure 5a**. The measurement setup, comprising a function generator for LED modulation and an Agilent SMU to record the photodetector electrical signal upon applying a negative bias, is depicted in **Figure S6a**. From **Figure 5a** it becomes obvious that upon increasing the modulation frequency, the photosensitivity decreases as the LED switching time $1/(2\pi f)$ does not suffice to allow the photocurrent to decay to its lowest value. From these measurements we extract the photocurrent attenuation (in dB) as a function of frequency (**Figure 5b**), from which a direct estimation of the $f_{3dB} = 1$ kHz can be deduced. Applying **Eqns. 5** and **6**, we calculate a rise time of $t_r = 350 \text{ }\mu\text{s}$ and a response speed of $\tau = 160 \text{ }\mu\text{s}$. This is in good agreement with an independent measurement of the rise time we performed upon modulating the LED with 100 Hz square pulse and recording the photocurrent signal through a 100 MHz oscilloscope (**Figure S6b**). The rise and fall times are calculated from **Figure 5c** as $t_r = 285 \text{ }\mu\text{s}$ and $t_f = 178 \text{ }\mu\text{s}$. We also measured the switching speed of the LED source at a frequency of 100 Hz and its rise and fall times were found to be similar and equal to $t_{r/f(LED)} = 160 \text{ }\mu\text{s}$. As a rule of thumb, a source with rise and fall times lower than at least 10% of those of the photodetector under test should be used. Since the fall time of the measured photodetector is very close to that of the LED, we infer that this measurement may not represent the intrinsic speed of our photodetector.

To address this issue, we employed transient photocurrent (TPC) technique to measure the device's response time more accurately. A nanosecond Nd-YAG laser source emitting at 470 nm with an incident pulse intensity of 2.8 mW cm^{-2} was used as per the experimental setup

shown in **Figure 5e**. The transient photocurrent plot is shown in **Figure 5f**. By fitting a monoexponential decay curve^[24] to this transient ($R^2 = 0.97$), an exponential time constant $\tau = 257 \pm 9$ ns was extracted. The values of $t_r = 105$ ns and $t_f = 512$ ns were also calculated from the same transient curve. The difference in the rise and fall time may be rationalised as the former is mainly limited by charge trapping/detrapping processes at the electrode interfaces and/or at the bulk of the film, while the fall time is additionally related to recombination processes and charge diffusion to the bulk of the perovskite layer.^[58] Charge generation and carrier transit are expected to be much faster processes, especially within the ultra-short-length channel. The response time values measured with TPC are three orders of magnitude faster than the ones measured previously using the much slower LED source and we consider the intrinsic speed of our photodetectors to lie within this range (hundreds of ns). This response speed is one of the highest reported in the recent literature for single layer coplanar photodetectors.^[7, 16, 17, 59] Note that faster response times below 200 ns^[24, 60] and even sub-ns^[26] response times have been reported (also measured using the TPC technique), albeit with vertical architecture multilayer perovskite photodetectors.

The response time can be further improved if we employ different electrode architectures with smaller widths (and thus area) and/or measure at lower illumination intensity. Another approach would be to decrease the series resistance of the device, for instance by employing certain trap passivation strategies^[61, 62] and by modifying the contacts with suitable self-assembled monolayers (SAMs) to decrease contact resistance^[63, 64] or simply by replacing the Al electrode with other metals, such as Titanium (Ti), the native oxide of which (TiO_x) is semiconducting as opposed to the insulating nature of AlO_x .

2.3 Flexible Photodetectors

Finally, we fabricated nanogap photodetectors on flexible indium tin oxide (ITO)-coated PET substrates. All devices were patterned via a-Lith to create interdigitated ITO-Al nanogaps with

a width of 7 cm. **Figure 6a** shows a photograph of an actual flexible substrate comprising several distinct devices, while **Figure 6b** displays the SEM micrograph of a representative ITO-Al nanogap photodetector. For all PET-based devices, the perovskite was deposited atop the patterned electrodes to form the flexible photodetector and illuminated with green light from the substrate/back side (**Figure 6c**). Optimised photodetectors showed similar photoresponse with similar devices fabricated on glass (**Figure 4**). The higher photocurrent ($0.15\ \mu\text{A}$ at $-1\ \text{V}$) is due to larger electrode width (7 cm). We do note however that the dark current is also higher ($3.41\ \text{nA}$ at $-1\ \text{V}$). Despite this, the calculated responsivity value remains high and around $33\ \text{A W}^{-1}$. Nevertheless, we emphasise the importance of being extra cautious with this value for the reason that, since the ITO electrode is fully transparent, the total area that is illuminated is higher than the nanogap area between the two electrodes that was used in the responsivity calculation. This means, charges are likely to be photogenerated far away from the nanogap electrodes and, owing also to the large diffusion length of the perovskite material (up to $2.9\ \mu\text{m}$)^[38, 46], they can be transported to the respective charge extracting electrodes, increasing thus the measured photocurrent.

3. Conclusions

In conclusion, we have demonstrated high-performance single-layer solution-processed mixed-cation lead mixed-halide perovskite photodetectors utilising coplanar Al-Au electrodes separated by nanogaps ($\approx 10\ \text{nm}$), developed on a variety of large-area substrates using a-Lith. By using asymmetric coplanar nanogap electrodes, we circumvent the limitations posed by commonly employed vertical structures, as the transit time of the photogenerated charge carriers is substantially reduced owing to the nanoscale interelectrode distance, leading to a faster response speed and low operating voltage. At the same time, upon varying the electrode widths, high photocurrents and responsivities were obtained. Because of the unique and extreme dimensionality, carefully engineered devices exhibited high responsivity ($\approx 33\ \text{A W}^{-1}$), specific

detectivity ($D^* = 10^{11}$ Jones) and fast photoresponse (≈ 260 ns); attributes which are remarkable for two terminal single-layer solution-processed photodetectors. Lastly, coplanar perovskite photodetectors were demonstrated on flexible plastic substrates utilising transparent ITO and opaque Al electrodes as the anode and cathode, respectively. It is noteworthy that the device fabrication was kept simple and fully compatible with low-cost printing manufacturing processes. Despite their semi-transparency and longer nanogaps, the devices demonstrated similar optoelectronic characteristics as those fabricated on glass, highlighting the tremendous potential of these coplanar perovskite photodetectors for exploitation in emerging forms of low-cost optoelectronics.

4. Experimental Section

Patterning of nanogap electrodes: Coplanar nanogap separated electrodes were patterned with adhesion lithography, using a process reported elsewhere.^[28, 33, 35, 52] In brief, Aluminium (Al) electrode with a thickness of 40 nm was thermally evaporated in high vacuum (10^{-6} mbar) on glass substrates and patterned to the desired design with photolithography. Then, the substrates were soaked in 1 mM solution of octadecylphosphonic acid (ODPA, Sigma Aldrich) in isopropanol (IPA) to form a self-assembled monolayer (SAM) on the Al surface, rendering it hydrophobic. Next, a global Gold (Au) electrode (35 nm) with a 5 nm Al underlayer to promote adhesion to the glass substrate, was deposited *via* thermal evaporation. In the case of the flexible substrates, an optically transparent Indium-doped Tin Oxide (ITO)-coated PET film (ITO with an approximately 30 nm thickness and resistance 50 ohms sq^{-1} , Visiontek Systems) served as the starting substrate. ITO was photolithography patterned and, after SAM functionalisation, 40 nm Al was thermally evaporated. In both cases, the next step was the application and subsequent removal of an adhesive film (First Contact, Photonic Cleaning Technologies). During this step, the metal in contact with ODPA had poor adhesion to the SAM-functionalised substrate and was removed when the adhesive glue was peeled off, while the strongly adhered

metal-on-substrate remained. As a result, a nanogap typically on the order of 10 nm was formed after removing the ODPa SAM *via* 10 min UV-ozone treatment.

Preparation of perovskite solution: To form the mixed-cation lead mixed-anion perovskite precursor solutions, caesium iodide (CsI, Alfa Aesar), formamidinium iodide (FAI, GreatCell Solar), lead iodide (PbI₂, TCI) and lead bromide (PbBr₂, Alfa Aesar) were prepared in the way corresponding to the exact stoichiometry for the desired FA_{0.83}Cs_{0.17}Pb[I_{0.9}Br_{0.1}]₃ compositions in a mixed organic solvent of anhydrous N,N-dimethylformamide (DMF, Sigma-Aldrich) and dimethyl sulfoxide (DMSO, Sigma-Aldrich) at the ratio of DMF : DMSO = 4 : 1.

Perovskite film deposition: The deposition of perovskite layers was carried out using a spin coater in a nitrogen-filled glove box with the following processing parameters: 5000 rpm (ramping time of 5 sec from idle) for 40 sec. 10 sec before the end of the spinning process, a solvent-quenching method was used by dropping 100 μ L anisole onto the perovskite wet films.

UV-Vis absorption spectroscopy: The perovskite thin film was deposited on quartz substrates, following the above-mentioned process. Measurements were performed using a Shimadzu UV2600 UV-vis spectrophotometer equipped with an ISR-2600 Plus integrating sphere. The film absorbance was calculated from the measured transmittance and reflectance data.

Scanning Electron Microscopy: All images were obtained with a FEI Inspect F SEM, and the cross-sections were prepared using a focused ion beam (FIB) in a FEI Quanta 3D ESEM. To prepare the cross-sections, first a layer of platinum was deposited using the Quanta's gas injection system. A 5 μ m deep trench is then milled through the platinum, using the FIB. The samples were then moved to the Inspect F for imaging. Imaging was conducted at two different accelerating voltages: top-down views were imaged at higher accelerating voltage (20 kV) to

show the electrode areas more clearly (brighter areas correspond to the gold electrode); cross-sections were imaged at lower accelerating voltages (5 kV) to reduce electron beam induced damage.

Atomic Force Microscopy: The surface morphologies of the films deposited from various precursor concentrations on the a-Lith patterned metal electrodes were obtained using an Agilent 5500 atomic force microscope (AFM) operated in tapping mode. Statistical and image analysis was performed using Gwyddion software.

Optical Microscopy: A Nikon Eclipse E600 POL optical microscope was used to image the films surface.

Photodetector electrical characterisation: Electrical characterization of the nanogap photodetectors was performed using an Agilent B2902A source-measure unit in a dry nitrogen atmosphere. LEDs with red, green and blue electroluminescence (EL) peaking at 632, 525, 475 nm, respectively, were employed and driven using a Keithley 2400 source meter unit. The illumination intensities generated by the LEDs when driven at different current levels were calibrated with a Thorlabs S120UV power sensor.

Photoresponse measurements: Dynamic characterization was performed by modulating the LED source with a square pulse at different frequencies *via* an Agilent 33220A function generator. The signal of the bottom-illuminated photodetector biased at a fixed voltage (usually -2 V) is either measured directly with an Agilent B2902A SMU or with an Agilent DSO6014A oscilloscope, amplified by a Stanford Research Systems SR570 current preamplifier. Transient photocurrent measurements were performed using an Nd-YAG pulsed laser tuned by an Optical Parametric Oscillator (OPO) to emit light at 470 nm with pulse duration of 3.7 ns at a repetition

rate of 10 Hz. A neutral density (ND) filter was used to adjust power intensity to 2.8 mW cm⁻² per pulse. The photogenerated carriers were transported to the electrodes by the build-in field (no external voltage was applied), and a 500 MHz Tektronix DPO3054 oscilloscope with an input resistor of 50 Ω was used to record the response curve through a Femto DHP-100 current amplifier. The detailed experimental setups are depicted in **Figure S6**.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the authors.

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Figures

Figure 1. a) Schematic illustration of a 3x3 array of coplanar Al/Au 10 nm-gap separated electrodes patterned with adhesion lithography. b) Photograph of a 2x2 cm glass substrate with 81 distinct coplanar nanogap electrode pairs. c) Side view schematic of the photodetector device structure depicting bottom illumination of the $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}[\text{I}_{0.9}\text{Br}_{0.1}]_3$ (FACs) perovskite film, deposited on top of the coplanar nanogap electrodes. d) Absorption spectrum of the FACs perovskite film deposited from a 2 M precursor solution and normalised electroluminescence (EL) spectra of the LEDs used to illuminate the perovskite photodetectors. e) Energy level diagram in a flat band configuration of the FACs perovskite energy levels and the Al-Au metal electrodes Fermi level energies. f) Operational mechanism of the FACs perovskite coplanar photodetector under electronegative bias: In the dark, if the applied bias is sufficiently high, charge carriers may tunnel through the Schottky barrier and be injected in the perovskite layer (blue circles), giving rise to the observed dark current (I_D). Under illumination, charge carriers are photogenerated in the perovskite layer (green circles) and transported to the respective electrodes, where they are collected and therefore contribute to a large degree to the total measured current under illumination (I_{ILL}). The net photocurrent (I_{PH}) is the difference of the $I_{ILL}-I_D$.

Figure 2. FACs perovskite film surface morphology characterisation. a-d) Atomic force micrographs of FACs perovskite films deposited from a) 0.25, b) 0.5, c) 1 and d) 2 M precursor solutions. Scale bar: 500 nm. e) Height distribution plot derived from the AFM images a-d) above. f) and g) Different magnification optical microscopy images of films derived from f) 0.25 M and g) 2 M precursor solution. h) Cross-sectional scanning electron microscopy (SEM) image of the film deposited from the most concentrated (2 M) precursor solution on the coplanar metal electrodes, depicting also its thickness.

Figure 3. Electrical characteristics of the FACS perovskite photodetectors fabricated with square-shaped Al-Au coplanar nanogap-separated electrodes. a) Semilogarithmic I-V curves of FACS perovskite photodetectors comparing films derived from varying concentration precursor solutions in the dark and under illumination with 525 nm green LED with an intensity of 1.67 mW cm^{-1} . b) Photodetector responsivity plotted as a function of perovskite precursor solution concentration at reverse and forward voltage of $\pm 2 \text{ V}$. c) Semilogarithmic I-V plot of the 2 M FACS perovskite photodetector characteristics in the dark under increasing illumination intensities at a wavelength of 525 nm. d) log-log plot of the photocurrent at -2.5 V vs light intensity derived by c) and linear fit to the experimental data ($R^2 = 0.999$).

Figure 4. FACS perovskite photodetectors fabricated with interdigitated Al-Au coplanar nanogap-separated electrodes. a) Optical microscopy image depicting the Al-Au interdigitated electrodes with interelectrode separation of 10 nm patterned with adhesion lithography and SEM image of the electrodes interface after deposition of the perovskite film from a 2 M precursor solution. b) Semilogarithmic I-V curves of FACS perovskite photodetectors fabricated with varying width interdigitated electrodes in the dark and under illumination with 525 nm green LED with an intensity of 1.67 mW cm^{-1} . c) Photocurrent vs dark current at -2 V as a function of electrodes width and linear fitting to the experimental values depicting also the slope of the fitted line. d) Photosensitivity vs voltage plot of the FACS perovskite photodetectors calculated from b) comparing the different electrodes width. e) Specific detectivity as a function of the electrodes' width calculated at reverse and forward voltage of ± 2 V.

Figure 5. Photoresponse of 2 M FAc's perovskite photodetectors fabricated with interdigitated 2 cm width Al-Au coplanar nanogap-separated electrodes. a) Photo-switching of the FAc's perovskite photodetectors (measured at -1 V) upon modulating the green LED source with frequencies 1 Hz to 1 kHz and light intensity of 0.9 mW cm^{-2} . b) Bode plot of photodetector photocurrent as a function of the LED's switching frequency. The dashed line defines the -3dB point, which determines the cutoff frequency (bandwidth). c) Photoresponse of the FAc's perovskite photodetectors (measured at -1 V) upon modulating the green LED source with frequency 100 Hz and light intensity of 0.9 mW cm^{-2} . The LED source and photodetector signals are measured with an oscilloscope. d) Determination of the rise (t_r) and fall (t_f) times from graph c). e) Experimental setup used to perform transient photocurrent (TPC) measurements. f) TPC signal recorded in photovoltaic mode fitted with a monoexponential decay function and calculated t_r and t_f .

Figure 6. Flexible FACs perovskite photodetectors. a) Photograph of an a-Lith patterned PET substrate depicting coplanar ITO-Al nanogap interdigitated electrode structures. b) SEM image of the ITO-Al nanogap electrodes interface. c) Photograph of the ITO-Al FACs perovskite photodetectors upon illumination with the green LED. d) Semilogarithmic I-V characteristics of the flexible FACs perovskite photodetectors fabricated with interdigitated 7 cm width ITO-Al coplanar nanogap-separated electrodes in the dark and under illumination with 525 nm green light with intensity of 1.67 mW cm^{-1} .

Table of Content

Flexible coplanar metal-perovskite-metal photodetectors are fabricated using nanogap separated asymmetric electrodes patterned with adhesion lithography. The ultra-short (≈ 10 nm) interelectrode distance and the carefully engineered perovskite film result in devices exhibiting high responsivity (33 A W^{-1}) and fast response times of 260 ns. The work showcases the high throughput fabrication of low-cost high-performing single-layer photodetectors on flexible substrates.

Keywords: nanopatterning, metal halide perovskites, photodiodes, image sensors

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High responsivity and response speed single-layer mixed-cation lead mixed-halide perovskite photodetectors based on nanogap electrodes manufactured on large-area rigid and flexible substrates

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Supporting Information

High responsivity and response speed single-layer mixed-cation lead mixed-halide perovskite photodetectors based on nanogap electrodes manufactured on large-area rigid and flexible substrates

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Figure S1. *I-V* characteristics of coplanar nanogap FACs perovskite photodetector in a linear scale. The photoactive perovskite layer was deposited from a 2 M precursor solution on top of interdigitated electrodes with a total width of 20 cm. Light intensity in all wavelength was 1.67 mW cm^{-1} .

Figure S2. a-c) SEM micrographs of FACs perovskite films derived from a) 1 M and b,c) 2 M concentration precursor solutions. The dependence of the film morphology on the solution concentration is evident as the 1 M film presents a sponge-like morphology, while the 2 M film is more compact comprising larger grains. When looking at the film surface with lower magnification in c), a wrinkled interconnected network may be discerned. This is also obvious from the optical micrograph shown in d), taken with a 50x magnification in dark field mode.

Figure S3. Cross-sectional a) TEM and b) SEM images of a FACs perovskite film deposited on the Al/Au electrodes. A nanogap size always <20 nm is clearly depicted.

Figure S4. Linear double voltage sweep of a representative FACs (1 M) perovskite photodetector device in the dark and under illumination (1.67 mW cm^{-1}).

Figure S5. Linear plot of the photosensitivity at -2.5 V vs light intensity calculated by the data shown in Figure 3c and linear fit to the experimental data ($R^2 = 0.999$).

Figure S6. Experimental setups used for the measurement of the photodetector speed in Figure 5a and 5c, respectively. a) The LED is driven with a square pulse of different frequency via an Agilent 33220A function generator and the signal of the bottom-illuminated photodetector device is measured with an Agilent B2902A SMU. b) The same setup is used for driving the LED (Agilent 33220A function generator), which is now connected to Channel 1 of an 100 MHz Agilent DSO6014A oscilloscope with an input resistor of 1 M Ω . The photodetector is negatively biased at a fixed voltage with the Agilent B2902A SMU and the output current is measured at the Channel 2 of the scope, amplified by a Stanford Research Systems SR570 current preamplifier.