Electronic Supplementary Material (ESI) for Nanoscale.

Electronic Supporting Information

Broadband-tunable spectral response of perovskite on paper photodetectors using halide mixing

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Methods:

Chemicals:

Nano graphite powder with 400 nm (PN: MKN –CG-400) average particle size was purchased at Lowerfriction Lubricants.

MAI, MABr (Greatcell Solar Materials: MS101000-10, MS301000-10), PbI_2, $PbBr_2$ and N,N-dimethylformamide (DMF) (Sigma Aldrich: 203602-50G, 398853-5G, 227056-1L).

Perovskite solutions

$MAPbX_3$ (X = I and Br) solutions were prepared by mixing MAX and PbX_2 with stoichiometric ratios (1:1). Subsequently, the precursor salts were dissolved in DMF by stirring at room temperature during 2 h approximately. The $MAPbI_3$ and $MAPbBr_3$ stock solutions were mixed in a (1−x)/x ratio to obtain the final solutions of $MAPb(I_{1-x}Br_x)_3$ (x = 0, 0.25, 0.5, 0.75, 1). All solutions were 1.67 M concentration and were prepared and kept in a N_2-filled glovebox.

Device preparation

a) Printing graphite contacts

The graphite contacts were printed applying the all-dry abrasion-induced deposition method. It is based on the rubbing of the graphite (or other van der Waals material) against the paper. The abrasion breaks the interlayer forces of the graphite and creates a film of interconnected platelets that covers the paper substrate. The rubbing was applied on graphite powder with a cotton swab on general copy paper.[1,2] See schematic of the process in Figure S1.

b) Drop casting perovskite solution:

The perovskite was deposited by drop casting 100 µL of the desired $MAPb(I_{1-x}Brx)_3$ (x = 0, 0.25, 0.5, 0.75, 1) solution on the area between the graphite contacts (see Fig 1.a.2-3). The device was dried at 60ºC during 1.5 h inside of a N_2-filled glovebox. During the first 25 min, the paper substrate was held with to microscope slides (1 mm thick) on the

borders, to avoid leakage of the perovskite solution from the contact of the paper with the hotplate. After 25 min, the paper substrate was placed in direct contact with the hotplate. After 50 min, the device was kept facing down to ensure the drying of the solution on the back side of the device. After 1 h 15 min it was flipped again to the initial position and finally left drying until 1 h 30 min (see Table S1).

Time (min)	Action
0	Placing paper substrate on hotplate at 60ºC. Holding the device with a 1 mm thick glass slide on each side. Adding slowly 100 µL of perovskite solution between the contacts.
25	Leave the sample in direct contact with the hotplate
50	Flip the sample, placing the top part in contact with the hotplate
75	Flip the sample again to the initial position
90	Take the sample out of the hotplate

TableS1. Steps for the development of the perovskite-on-paper devices.

Transmission and photoluminescence (PL) measurements.

For these measurements we deposited the perovskite solutions on paper without graphite and let the sample dry following the same steps as described in Table S1. For transmission measurements we used a Halogen Lamp (LHS-H100C-1) light source and the light transmitted by the resulting samples was recorded using an imaging spectrograph (Princeton Instruments, SpectraPro HRS-300, ProEM HS 1024BX3). For the PL measurements we used a pulsed laser diode (λ_{ex} = 405 nm, PicoQuant LDH-D-C-405, PDL 800-D) with a 40 MHz laser repetition rate and a laser fluence of 500 nJ cm^{-2}. We recorded the resulting PL spectra with the previously mentioned spectrograph. A pulsed laser source was chosen to reduce light induced phase segregation.[3]

Material	Electrodes	Responsivity (mA/W)	I_{ON}/I_{OFF}	t_{ON}/t_{OFF} (ms)	Reference
$CsPbBr_3$ microcrystals/paper	Graphite-pencil-drawn	2100 @9V	~10^3	0.25 / 0.45	[4]
$MAPbBr_3$/paper	Au electrodes	1300 @1V	10^4	11 / 21	[5]
$MA_{0.6}FA_{0.4}PbI_3$/paper	Cu/Cr/Au	270 @5V	-	-	[6]
2D CsPbBr3-MXene/paper	MXene	44.9 @10V	2.3x10^3	48 /18	[7]
Origami $MAPbI_3$/paper	Graphite-pencil-drawn	4.4 @5V	32	< 10 / < 10	[8]
$MAPbBr_3$/paper	Graphite, all-dry abrasion	423 @30V	16	77 / 113	This study
$MAPbBr_3$/paper	Graphite, all-dry abrasion	0.57 @1V	3.26	130 / 240	This study

Table S2. Device performances of the reported perovskite-on-paper devices.

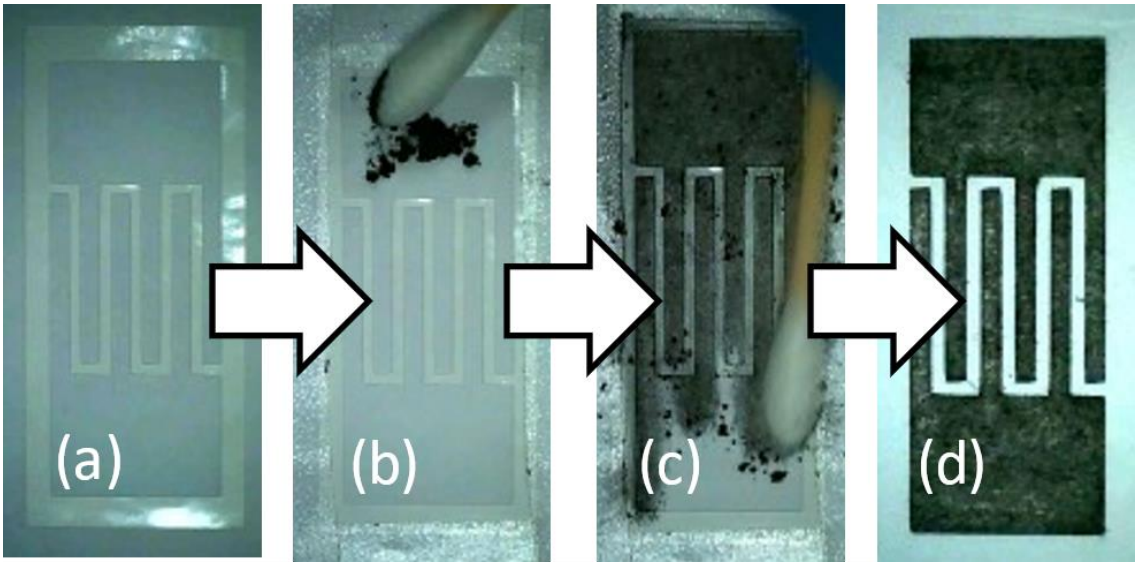

Fig. S1. Preparation of graphite contacts on paper. (a) Copy paper with a vinyl stencil mask with device layout. (b-c) Deposition of graphite powder and rubbing until complete covering of the mask. (d) Resulting graphite on paper substrate ready for the next steps of the device preparation.

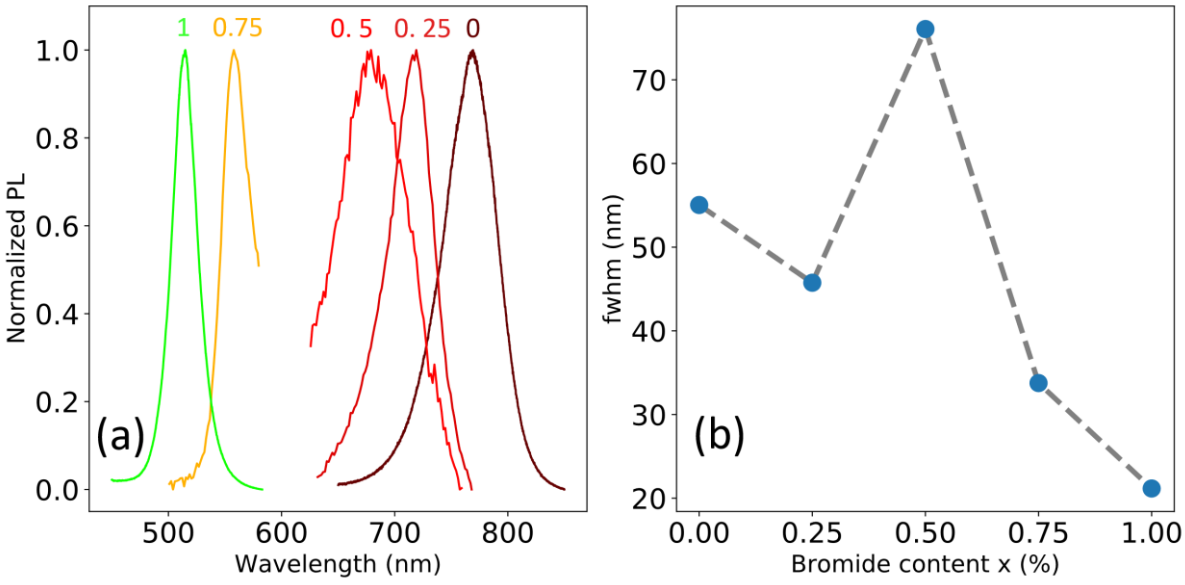

Fig. S2. (a) Measured PL spectra of each perovskite composition, there is observed a clear bandgap variation. (b) Full width at half maximum (fwhm) of each PL spectrum vs bromide content.

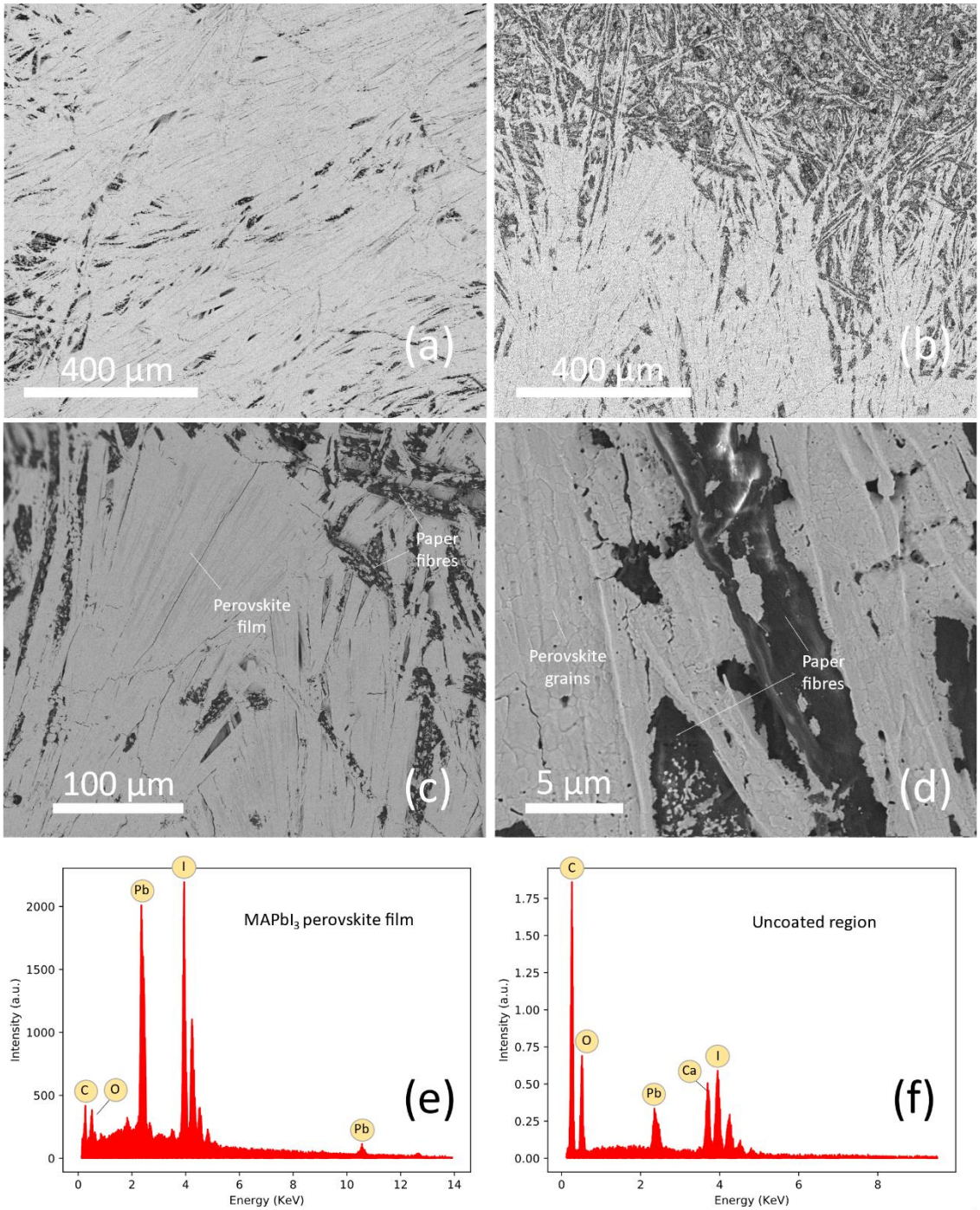

Fig. S3. SEM images and EDX results of $MAPbI_3$ perovskite-on-paper device surface. (a) Region covered by a homogeneous and mostly continuous perovskite film**.** (b) Place with a more predominant of uncoated paper fibres. (c-d) Zooming in the devices surface for a more detailed observation of the perovskite film and paper fibres. EDX results from the regions denoted in images (c) and (d) confirm the chemical compositions of $MAPbI_3$ (e) and of copy paper (f).

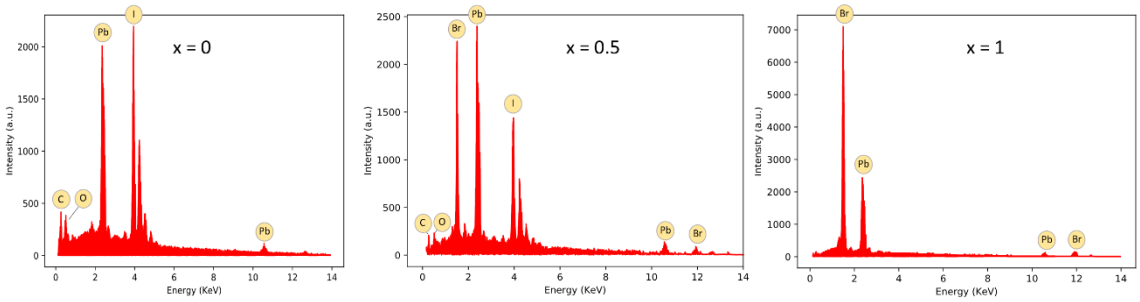

Fig. S4. EDX results of x = 0, 0.5 and 1 samples.

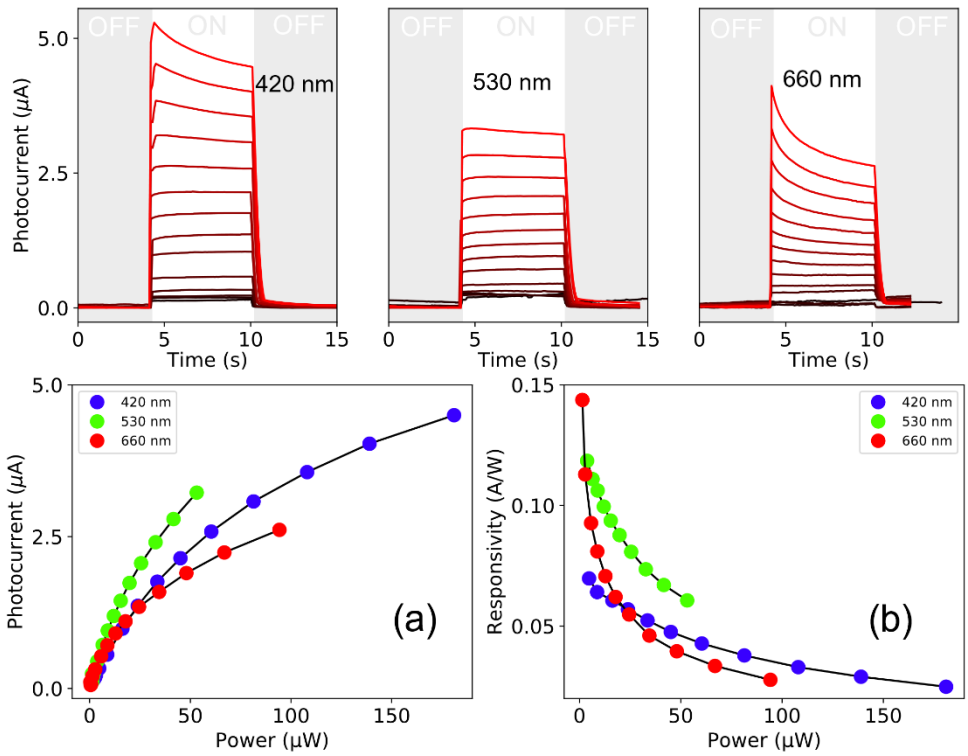

Fig. S5. $MAPbI_3$ device. Photocurrents generated at increased illumination intensities when exciting with λ_{LED} = 420, 530 and 660 nm. (a) and (b) Photocurrent and responsivity dependence on the illumination intensities for the different λ_{LED}.

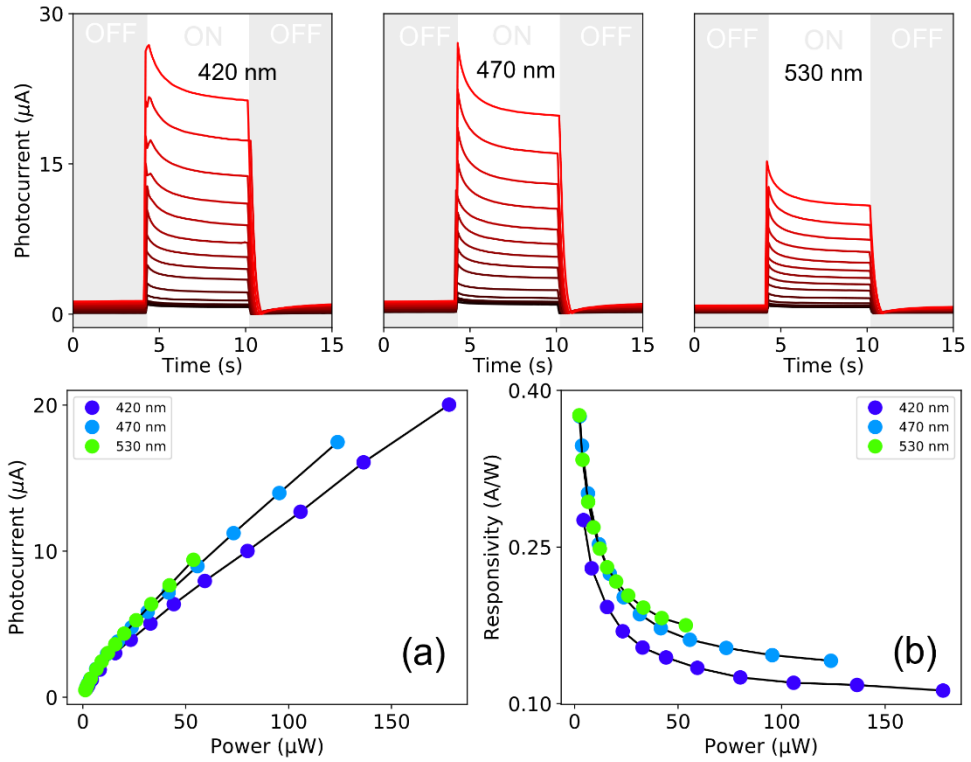

Fig. S6. $MAPbBr_3$ device. Photocurrents generated at increased illumination intensities when exciting with λ_{LED} = 420, 470 and 530 nm. (a) and (b) Photocurrent and responsivity dependence on the illumination intensities for the different λ_{LED}.

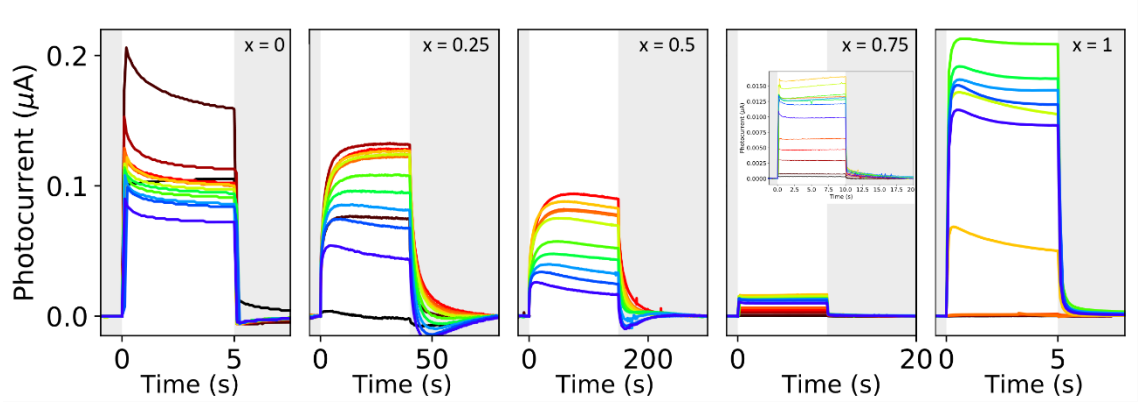

Fig. S7. Photocurrents generated on the x = 0, 0.25, 0.5, 0.75 and 1 samples when illuminating with the different LEDs. Each colour depicted is the associated to the corresponding of the incident LED light. Inset: x = 0.75 photocurrents zoomed in.

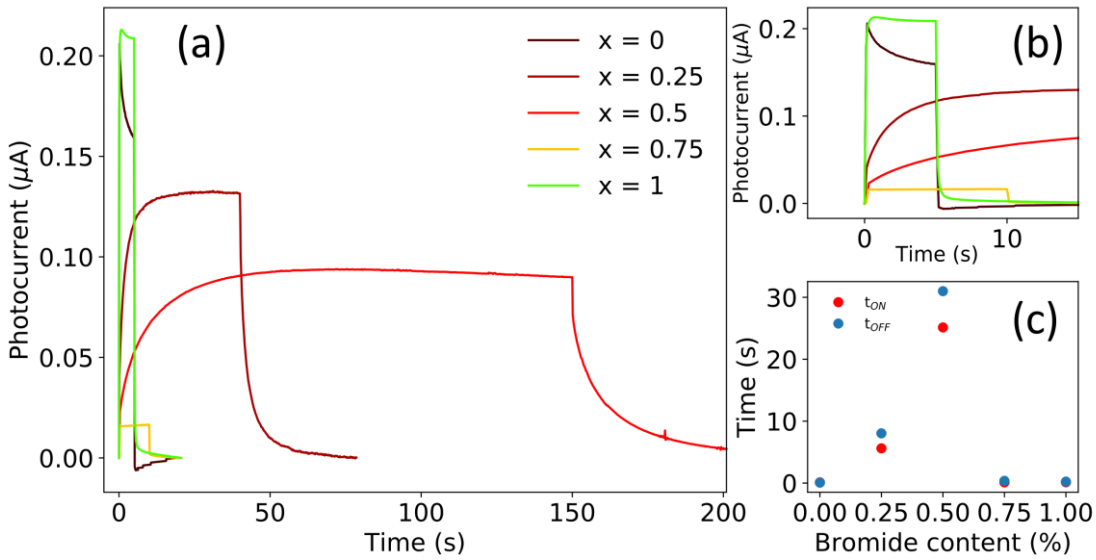

Fig. S8. (a) Maximum photocurrents of each device, each color depicts the incident LED color. All measurements were at illumination intensity of 0.365 mW (5 μW/mm^2) and the bias voltage of operation of 1 V. (b) Zooming in the initial times of the device response. (c) the rise (t_{ON}) and decay (t_{OFF}) times of each device.

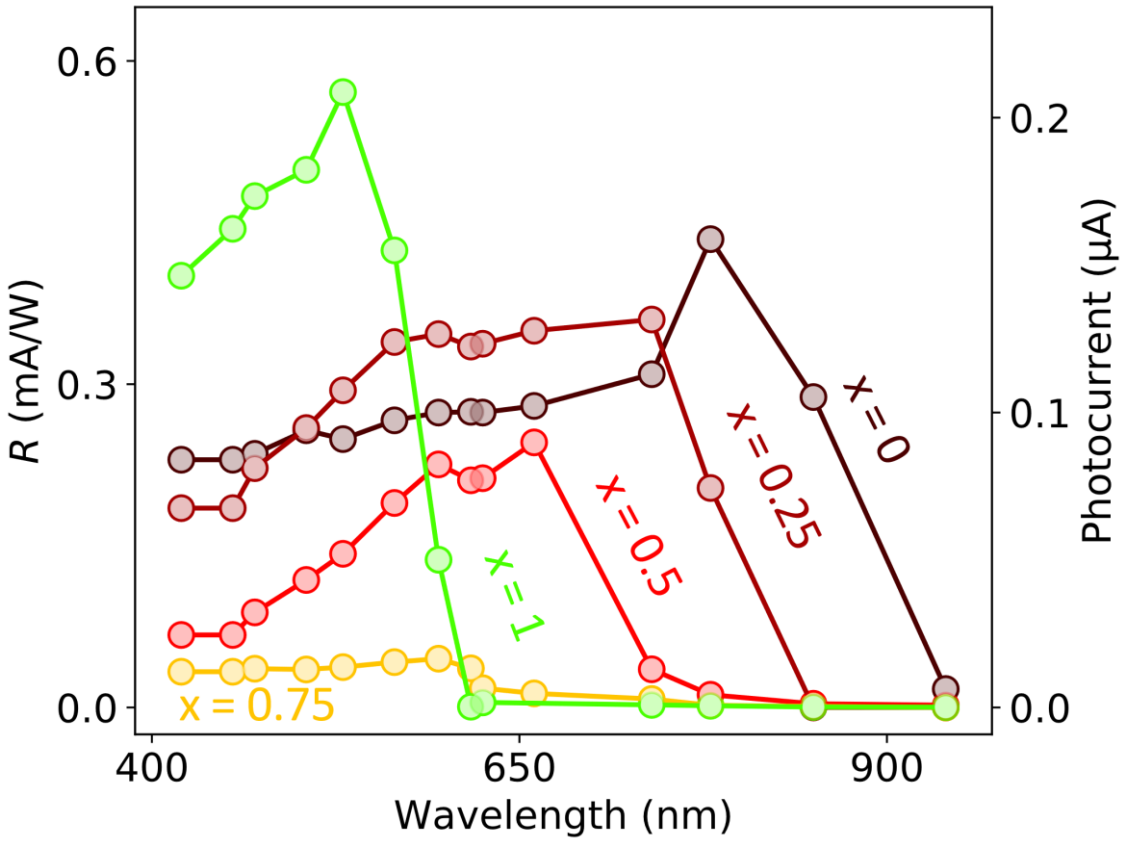

Fig. S9. Responsivities and photocurrents of the different devices when exposed to LED lights of different wavelengths at a constant illumination intensity of 0.365 mW (5 μW/mm^2) and operation voltage of 1 V. The depicted colours are related to the maximum *R* wavelength positions.

References

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