Supporting Information

Strong Photocurrent from Two-Dimensional Excitons in Solution-Processed Stacked Perovskite Semiconductor Sheets

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METHODS

**Device Fabrication:** The 2D inorganic-organic perovskite \((\text{C}_6\text{H}_9\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbI}_4\) is used as the photoresponsive material in all configurations. For configuration 1, pre-cleaned, patterned transparent ITO (indium tin oxide) coated glass slides are used as the anode, onto which CHPI (40 mM solution/N,N-dimethylformamide) is spin-coated at 2000 rpm for 60 sec (film thickness ~800 nm) and then annealed in air at 60 °C for 10 mins. The cathode is made by thermally evaporating aluminium (Al) or gold (Au) (thickness ~100 nm) on top of the CHPI/ITO substrate to complete this configuration 1 [Al/CHPI/ITO or Au/CHPI/ITO] (Figure 1c). The photodetector configurations (2 and 3, Figure 6a,c) using CHPI as the active absorbing layer are fabricated utilizing a TiO\(_2\) compact layer, with a mesoporous TiO\(_2\) scaffold layer (Dyesol, <50 nm particle size) in the case of 3, as the electron transport layer (ETL) and 2,2’,7,7’-tetrakis-(N,Ndi-p-methoxyphenylamine)9,9’-spirobifluorene (spiro-OMeTAD, Sigma Aldrich) as the hole transport layer (HTL). A 50 nm thin compact layer of TiO\(_2\) (c-TiO\(_2\)) was deposited on the F-doped SnO\(_2\) (FTO) coated glass by spin-coating (1500 rpm/60 sec) from a mildly hydrochloric acidic solution (2 M) of titanium isopropoxide in dry ethanol. Subsequently the films were heat treated at 500 °C for 30 mins in air and left to cool to room temperature. CHPI solution (40 mM/N,N-dimethylformamide) was spin coated (2000 rpm/60 sec) onto the c-TiO\(_2\)/FTO substrate in air and substrates were annealed at 60 °C for 10 mins. The hole transport material, spiro-OMeTAD, was then spin-coated from a chlorobenzene solution (including lithium bis(trifluoromethylsyfonyl) imide salt and tert-butylpyridine as additives) (2000 rpm/45 sec) on the CHPI/mp-TiO\(_2\)/c-TiO\(_2\)/FTO substrate. Finally, gold counter electrodes (~ 90 nm) were deposited by thermal evaporation to get the photodetector planar heterojunction configuration 2 [Au/spiro-OMeTAD/CHPI/c-TiO\(_2\)/FTO]. In configuration 3 an additional mesoporous TiO\(_2\) (mp-TiO\(_2\) ~500 nm) layer was spin-coated (1500 rpm/60 sec) using TiO\(_2\) paste (prepared in dry ethanol) on top of the c-TiO\(_2\) layer. Prior to CHPI deposition, the sample was calcined at 500 °C for 1 hour to remove
any organic overlayer. The remaining layers of CHPI, spiro-OMeTAD and Au electrodes were deposited in the same way as described above to obtain configuration 3 [Au/spiro-OMeTAD/CHPI/mp-TiO2/c-TiO2/FTO]. The effective area of all fabricated configurations (1, 2 and 3) was kept fixed to 9 mm².

For scanning photocurrent experiments, a thin CHPI film (100 nm) is fabricated by intercalating the organic moiety (C₆H₉C₂H₄NH₃I) into a thin PbI₂ film. On top of the CHPI film, Al finger contacts (150 nm thick) with a separation of 900 μm are deposited by thermal vapour deposition.
Figure S1. (a) Room-temperature static wide-range (300-1100nm) photocurrent spectral response of CHPI in configuration 1 under 0 V bias. The Transmission spectrum (blue dotted line, right axis) of the bare ITO substrate is also included for comparison. Only below 350 nm does the ITO absorption edge mask all photocurrent and no significant photocurrent is observed beyond 600 nm. (b) Illumination power dependence of band-to-band photocurrent response for configuration 1 at 410 nm excitation under +5 V, -5 V and 0 V applied bias.
Figure S2: (A) Bias dependent photocurrent spectra of CHPI in configuration 1 (as in Figure 4a), with (B) corresponding simulated photocurrent spectra, assuming two Gaussian contributions of band-to-band (~475 nm) and exciton (~525 nm) components, shown in Figure (C).
In order to better distinguish the different contributions to the photocurrent we use singular value decomposition (SVD) which again identifies two main components (Figure S3a,b). The first component (SVD1) follows the linear absorption spectral profile with strong excitonic contributions at the absorption edge. This component shows a linear variation with external bias (Figure S3d). Additionally we find a second ten-fold weaker component (SVD2), which follows the first derivative of SVD1 (Figure S3c). This component shows a strong dependence on voltage until +1.0 V, after which it saturates (Figure S3d). Based on the spectral shape and voltage dependence, we attribute this second component to a modulation of...
the photocurrent spectrum. This modulation can be explained by an initial build-up of photogenerated charge carriers at either side of the device, due to inefficient extraction at low voltages. Once the external field reaches sufficiently high values, extraction becomes more efficient and the field saturates. This interpretation matches with the band bending at CHPI-electrode interfaces explained in the section 2.2.

The Singular value decomposition (SVD) function in Matlab programme has been utilised in SVD analysis, which takes the data as a 3D matrix and tries to decompose it into vectors. SVD describes the concept in linear algebra of factorisation of a matrix, which yields its singular vectors. In our case we took the voltage as one dimension, the wavelength as a second, and photocurrent as third. The photocurrent data was then decomposed in vectors which had the same spectrum and the same voltage dependence.

In our case the input matrix $PC_{ij}$ is a photocurrent (PC) matrix of our photovoltaic devices with the first dimension as the variation of PC with excitation wavelength $\lambda$, and the second dimension as the variation of PC with voltage $V$.

$$PC_{ij} = \begin{pmatrix}
PC(\lambda) & PC(V) \\
\end{pmatrix}$$

We use the built-in function ‘svd’ in Matlab to decompose the matrix into its components. One of the obtained matrices defines the spectral components of the photocurrent, which we label ‘SVD component 1,2,…’, while the other matrix defines the variation of these components with voltage.
Figure S4: Photocurrent spectral response recorded for mixed IO perovskite films of 
(C$_6$H$_9$C$_2$H$_4$NH$_3$)$_2$PbI$_{(4-y)}$Br$_y$ at $y=0.00$ and $y=0.25$ under applied bias voltage of 1 V. The 
exciton absorption peak compositional tunability of these mixed IO perovskites has been 
previously reported$^{25}$ at 508nm ($y=0.0$), 482nm ($y=0.25$), 458nm ($y=0.50$), 398nm ($y=0.75$) 
and 388nm ($y=1.00$).
Figure S5: Glancing angle thin film X-ray diffraction pattern of thin CHPI film deposited on FTO/c-TiO$_2$/mp-TiO$_2$ substrate. Strong (001) peak signifies the presence of the alternate inorganic and organic layering of 2D perovskite inside the TiO$_2$ meso-porous scaffold. The X-ray diffraction pattern is compared with a CHPI intercalated film$^{26}$ to show position of all (00l) planes.
Figure S6: Room-temperature (a) transient photocurrent response of another 2D perovskite, MPPI [(C₆H₅CH(CH₃)CH₂-NH₃)₂PbI₄] in configuration 3 under periodic ON/OFF illumination of 410 nm and 508 nm excitations at 0 V bias, and (b) Photocurrent spectra recorded under different applied bias potentials.