Supporting Information

Lattice Marginal Reconstruction Enabled High Ambient-Tolerance Perovskite Quantum Dot Phototransistors

Shijie Zhan,[a] Xiangbin Fan,[a] Jiangbin Zhang,[b,c] Jiajie Yang,[a] Sang Yun Bang,[a] Soo Deok Han,[a] Dong-Wook Shin,[a] Sanghyo Lee,[a] Hyung Woo Choi,[a] Xiaozhi Wang,[d] Bo Hou,[*a,e] Luigi G. Occhipinti,[*a] and Jong Min Kim,[a]

[a.] *Electrical Engineering, Department of Engineering, University of Cambridge, Cambridge, CB3 0FA, UK*
E-mail: lgo23@cam.ac.uk
[b.] *Cavendish Laboratory, Department of Physics, University of Cambridge, Cambridge CB3 0FA, UK*
[c.] *College of Advanced Interdisciplinary Studies, National University of Defense Technology, Changsha 410073, P. R. China.*
[d.] *College of Information Science and Electronic Engineering, Zhejiang University, Hangzhou, 310058, China*
[e.] *School of Physics and Astronomy, Cardiff University, Cardiff, CF24 3AA, Wales, UK*
E-mail: HouB6@cardiff.ac.uk

Perovskite Quantum Dot Synthesis

All chemicals were purchased from Sigma Aldrich without any further purification. Typically, lead bromide ($PbBr_2$, 0.4 mmol) and caesium bromide (CsBr, 0.4 mmol) were dissolved in dimethylformamide (DMF, 10 mL). Oleic acid (OA, 1 mL) and oleylamine (OAm, 0.5 mL) were added to stabilize the precursor solution. OA and OAm were dried under vacuum at 100 ℃ before loading into the reaction solution. Then, 0.1 mL of the precursor solution was quickly added into anhydrous octane (10 mL) under vigorous stirring. Strong blue emission was observed immediately after the injection.

InGaZnO Thin Film Transistor Fabrication

Before deposition of perovskite quantum dot (PeQD) onto the oxide channel, the InGaZnO TFT was fabricated. Bottom gate top contact structure was adopted in this work using doped p-type Si wafers with a thermally grown 200 nm SiO_2 dielectric layer as substrate. Before InGaZnO sputtering, substrates were thoroughly cleaned with acetone and isopropyl alcohol (IPA) in a sonication bath for 10 minutes, and then dried by N_2. Amorphous InGaZnO (In_2O_3: Ga_2O_3: ZnO = 2:1:2 at weight percentage) was deposited on the cleaned substrates through RF sputtering. In the sputtering process, RF power, Ar flow, chamber pressure, substrate temperature and film thickness were fixed at 75 W, 25 sccm, 6.5 mtorr, room temperature and 30 nm, respectively. Then InGaZnO films were patterned through wet etching using 1% HCl solution in deionized water. A top contact of 10 nm Ti/100 nm Al was deposited by an e-beam evaporator after the photolithography process. Afterwards, the devices were baked at 150 ^oC for 1 hour under an ambient condition.

Photoresponsivity Measurement

Before measurement, all devices were stored in the dark and ambient environment with the temperature and humidity at 24.8℃ and 40%. Transfer curves of the phototransistors were measured using Keithley 4200 Semiconductor Analyzer under light sources with different wavelength and power density. For the mapping of photoresponsivity, the phototransistor was shined by a 475 nm-light at 7.73 $\mu W/cm^2$

with both the gate and drain voltage scanning from minimum to maximum values. For both of the wavelength and power dependent measurement, the gate and drain voltage were bias with 0 V and 15 V, respectively.

Lifetime Monitoring

After device fabrication, the original photoresponsivity was measured after the devices were exposed in ambient for ~1 hour, which was regarded as the base of comparison. Afterwards, one device was put in the ambient condition with the humidity 40% while the other device was stored in a sealed box with additional water inside to reach 80% humidity. The temperature of both conditions is ~24.8 ℃. The water in the box with higher humidity will be adjusted every day according to data shown in the humidity sensor inside to keep the humidity level ~80%. For the lifetime measurement, the transfer curves of phototransistors were tested after a certain period of time to extract the photoresponsivity. Compared with the original value, the decay of photoresponsivity can be extracted.

Transmission Electron Microscopy

The sample was prepared by casting one drop of diluted PeQD solution with 0.5mg/ml in octane onto Cu grids. For the AcOEt treated one, the Cu grid with PeQDs was dipped in AcOEt for 40 s. Then both of the grid was annealed at 100℃ and dried in vacuum chamber for 4 hours before the TEM experiment.

Atomic-resolution aberration-corrected high annular dark-field scanning transmission electron microscope (HAADF-STEM) and elemental mapping were conducted on a JEOL ARM-200F at 200 KV (cold field emission source Cs probe corrected). The electron diffraction, brightfield, and dark-field transmission electron microscopy images were conducted on JEOL JEM-3000F field emission gun TEM at 300 KV with a camera length of 255.8 mm.

Photoresponsivity Calculation

The photoresponsivity is calculated according to the following equation:

$$Photoresponsivity\ (A/W) = \frac{Photocurrent\ (A)}{Light\ power\ on\ active\ area\ (W)}$$

Here, 475 nm light-source is adopted where the power density of incident light is 7.75 μW/cm^2. The devices have active area of 720 μm × 20 μm. Photocurrent is the subtraction of drain current under illuminance and dark current.

Statistical Ratio Counting

The ratio of rectangle and truncated PeQDs are counted in Fig. S8a (red-dotted area) and Fig. S8b for untreated PeQDs, and in Fig. S8e and Fig. S8f for treated ones. Due to the obscureness at some part of images, the shape-uncertainty of some nanocrystals, we conducted several counting for each image and calculated the average results for untreated and treated ratio, respectively, as the value of bar. The error values were determined by the maximum and minimum value during counting.

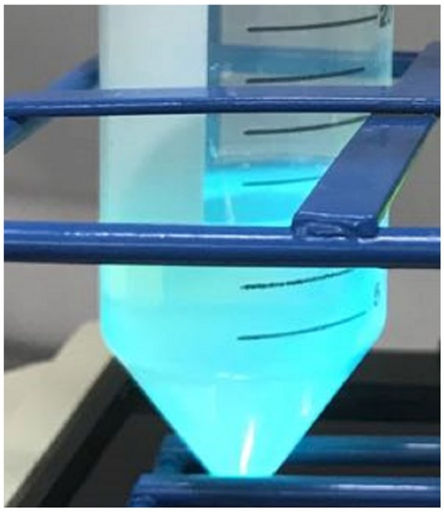

Fig. S1 The fluorescence image of the synthesized blue PeQD solution.

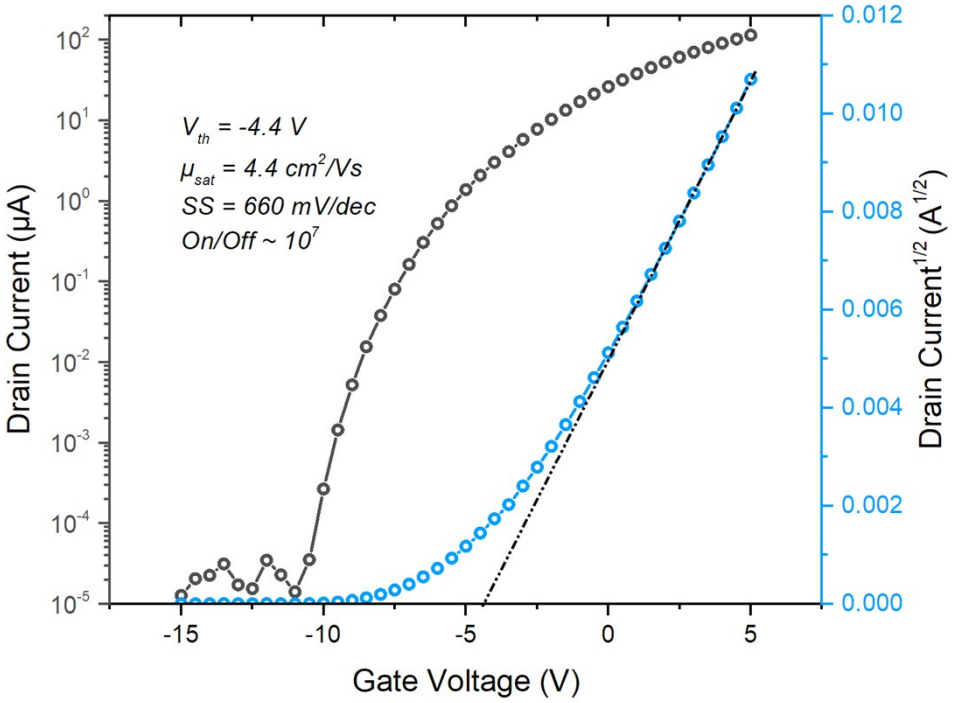

Fig. S2 The transfer curve of a typical InGaZnO TFT shown either in a log scale or a square-root-linear scale. The figure of merit performance is listed in the figure, including threshold voltage (V_{th}), saturated mobility (μ_{sat}), subthreshold swing (SS), and on-current/off-current ratio (On/Off).

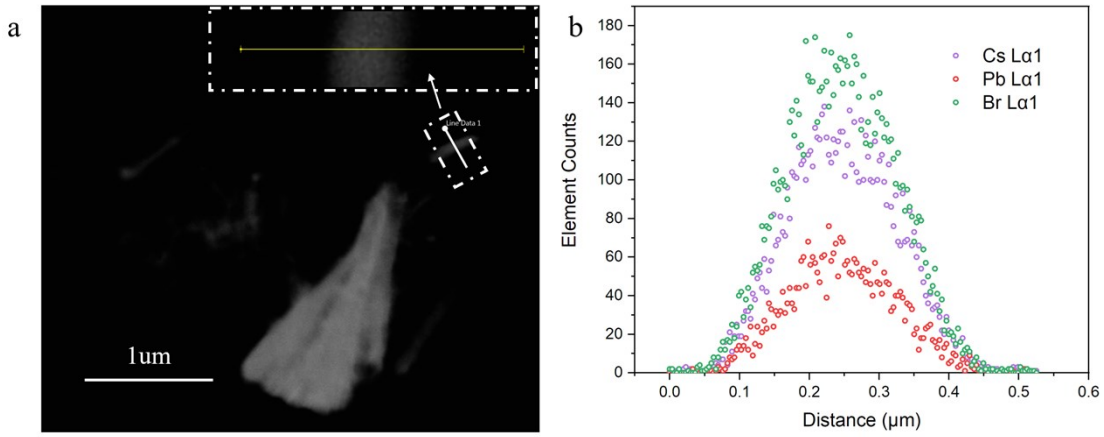

Fig. S3 Line-scan EDX mapping of a PeQD film. (a) The TEM image of the PeQD film with the line-scanned area marked with white dotted line. The inset figure is the enlarged image for the line-scanned area. (b) EDX mapping of Cs, Pb and Br across the line-scan area. The ratio of Pb and Br is 1:3 according to the element count.

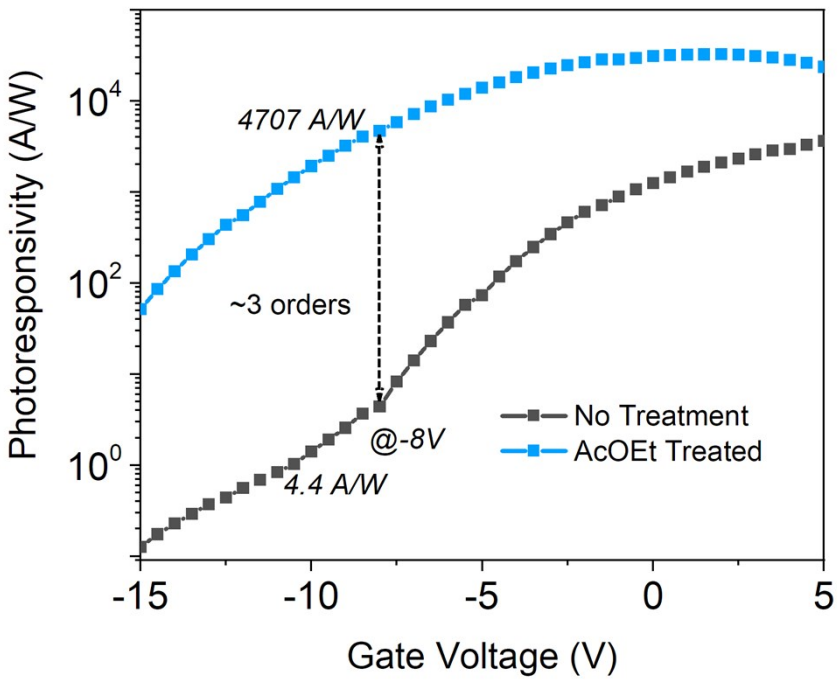

Fig. S4 Photoresponsivity versus gate voltage plot before and after AcOEt treatment with incident wavelength and power density at 475 nm, and 7.73 μW/cm^2 (V_{DS} = 15 V). Significant enhancement of the photoresponsivity was found, with 3 orders of magnitudes when gate voltage is -8 V.

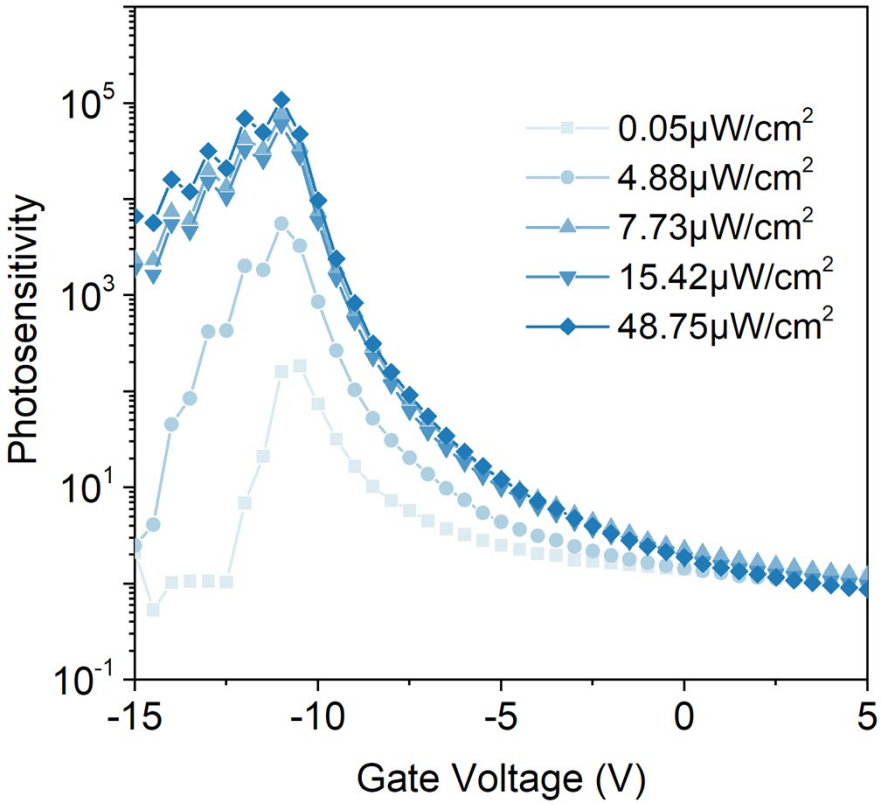

Fig. S5 Photosensitivity of the AcOEt-treated PeQD hybrid phototransistor under different power density of the incident light (475 nm). V_{DS} = 15 V.

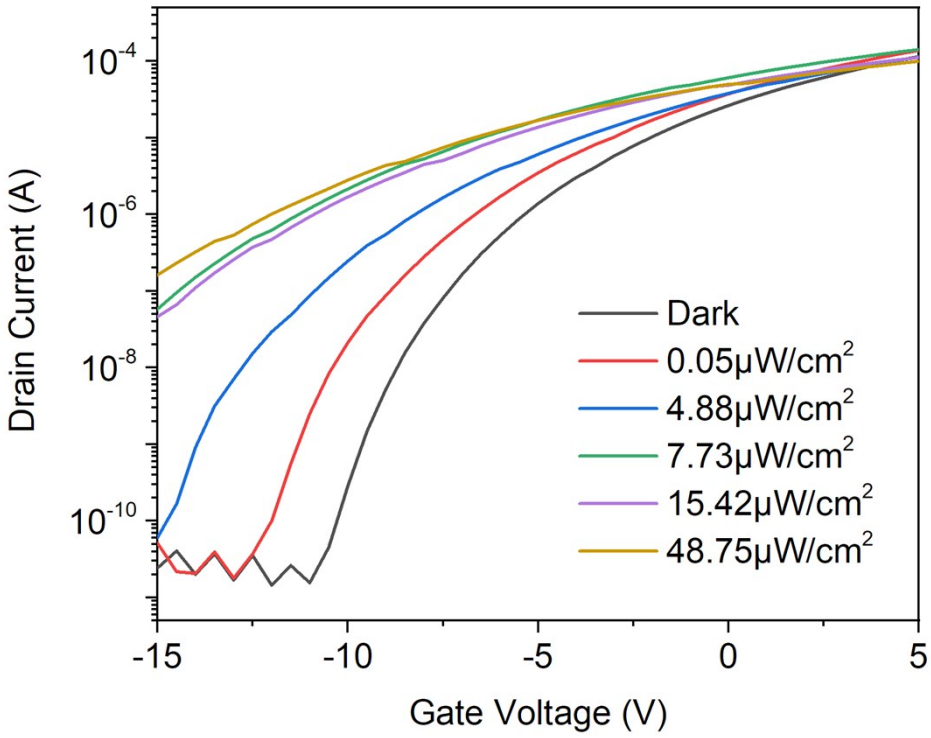

Fig. S6 The transfer curve of the AcOEt-treated PeQD/InGaZnO phototransistor with different power density of incident light (475 nm). V_{DS} = 15 V.

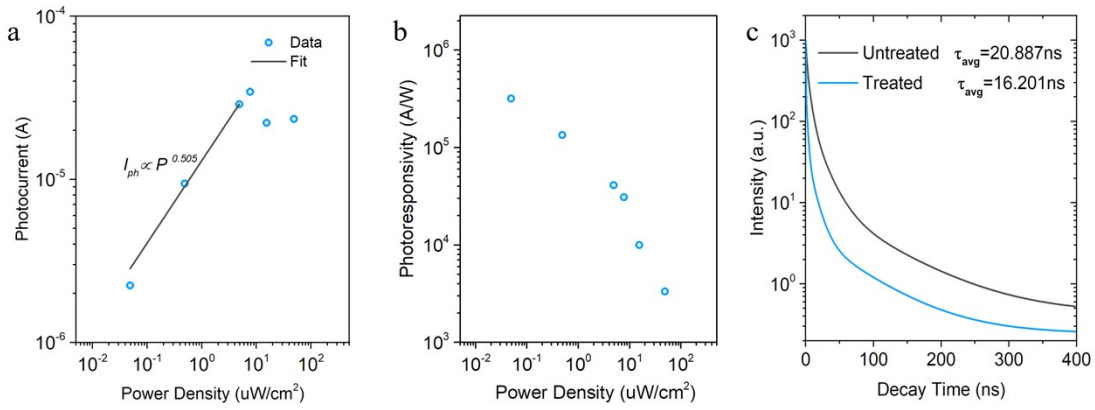

Fig. S7 (a) Power-dependent photocurrent and (b) photoresponsivity of the AcOEt-treated phototransistor. The incident-wavelength is 475 nm. Here V_{GS} = 0 V and V_{DS} = 15 V. (c) Time-resolved PL of the untreated and treated PeQD films. The inset legend shows the corresponding exciton lifetime extracted using multi-exponential decay formula with three decay processes.

	Untreated	**Treated**
t_1	1.609 ns	0.3995 ns
t_2	5.38 ns	2.169 ns
t_3	18.15 ns	10.89 ns
t_4	83.68 ns	71.34 ns
A_1	9090	19290
A_2	8191	4155
A_3	2081	721.1
A_4	203.4	73.71
t_avg	20.8877	16.2013

Table. S1 Lifetime constant and relative intensity of the untreated and treated PeQD films based on the four-exponential-decay model.

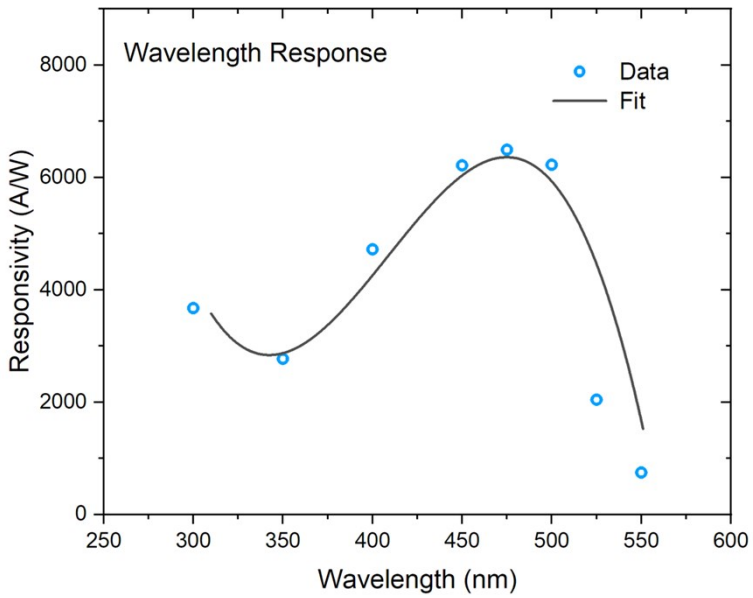

Fig. S8 Wavelength-dependent photoresponsivity of the AcOEt-treated phototransistor. In this measurement, V_{GS} = 0 V and V_{DS} = 15 V.

Material & Structure	Responsivity (A/W)	Sensitivity	Wavelength (nm)	Reference
DNTT / $CsPbBr_3$	1.7×10^4	8.1×10^4	460	*1*
$CH_3NH_3PbI_{3-x}Cl_x$ / PEDOT:PSS	7.6×10^8	/	895	*2*
$CsPbI_{3-x}Br_x$ / MoS_2	7.7×10^4	$\sim 10^4$	532	*3*
$CsPbI_3$ / DPP-DTT	1.1×10^2	6×10^3	405	*4*
CsPbBr3 (PMMA) / InGaZnO	1×10^3	/	512	*5*
$FAPbBr_3$ / Graphene	1.1×10^5	<2	520	*6*
$MAPbI_3$ / SnO_2	1.83×10^3	2.7×10^3	655	*7*
$CsPbBr_3$ / InGaZnO	5.4×10^4	$\sim 10^5$	475	*This work*

* *PeQD: perovskite quantum dot*; *PEDOT:PSS: poly(3,4-ethylenedioxythiophene) polystyrene sulfonate*

DNTT: dinaphtho[2,3-b:2',3'-f]thieno[3,2-b]thiophen; DPP-DTT: diketopyrrolopyrrole-dithieno[3,2-b]thiophene

FA: formamidinium; MA: methylammonium

Table. S2 Summary of the performance for PeQD-based hybrid phototransistors developed in recent years.

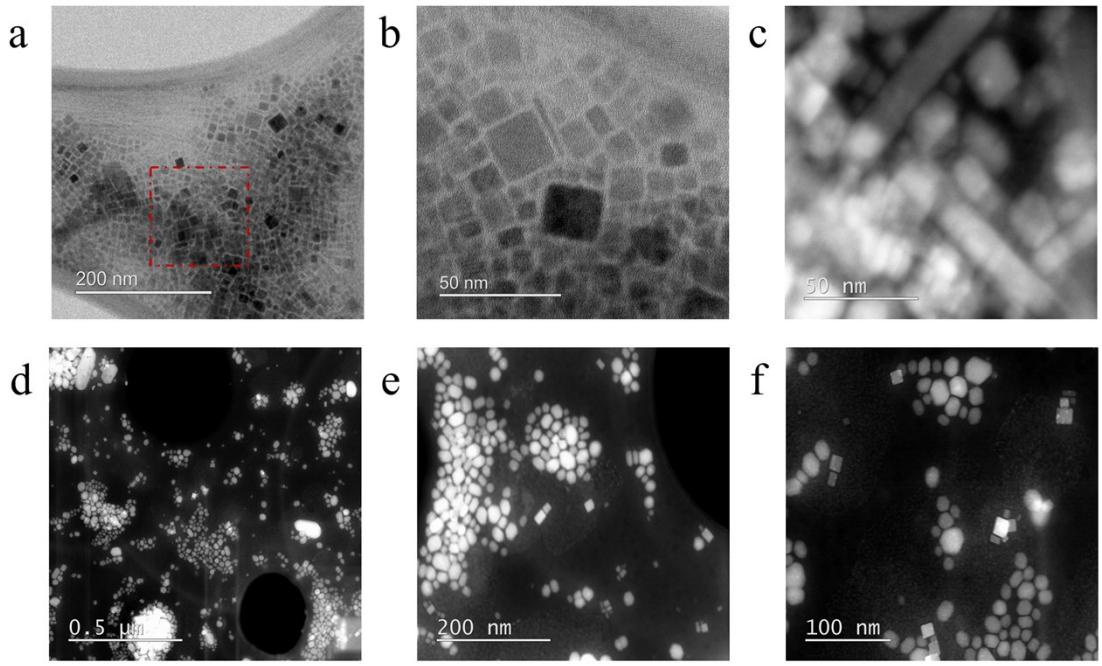

Fig. S9 (a) The TEM image of untreated PeQDs with a scale of 200 nm. (b) The TEM image of untreated PeQDs with a scale of 50 nm. (c) The STEM image of untreated PeQDs with a scale of 50 nm. The low resolution is caused by the high density of surface ligands on the PeQDs. (d)~(f) The STEM image of treated PeQDs with a scale of 500 nm, 200 nm, 100 nm. The nanocrystal counting area includes: the red-dotted area in (a), whole images of (b)(e)(f).

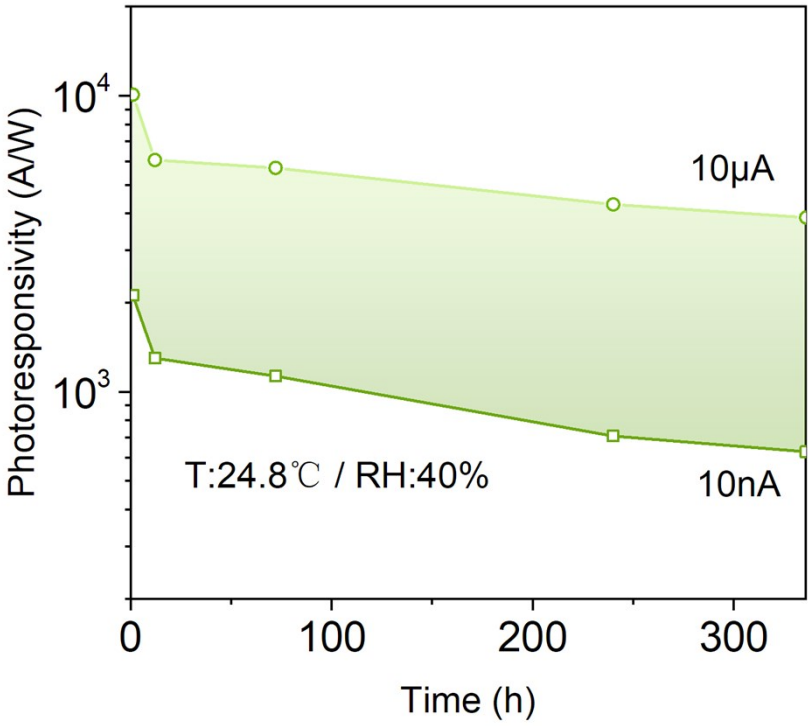

Fig. S10 Photoresponsivity lifetime of the AcOEt-treated hybrid phototransistor under the ambient condition with a drain current of 10 μA or 10 nA. The trend of photoresponsivity decay under different drain current is consistent.

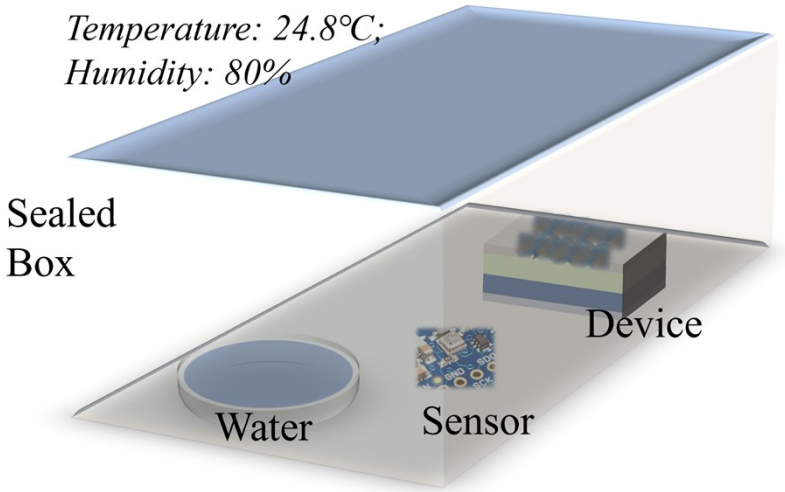

Fig. S11 The setup for stability test of the AcOEt-treated PeQD hybrid phototransistor. An amount of water was put in a petri dish to control the humidity level in the sealed box. A humidity and temperature sensor were put inside to monitor the inner condition. RH 80% is the highest humidity level feasible in this set up.

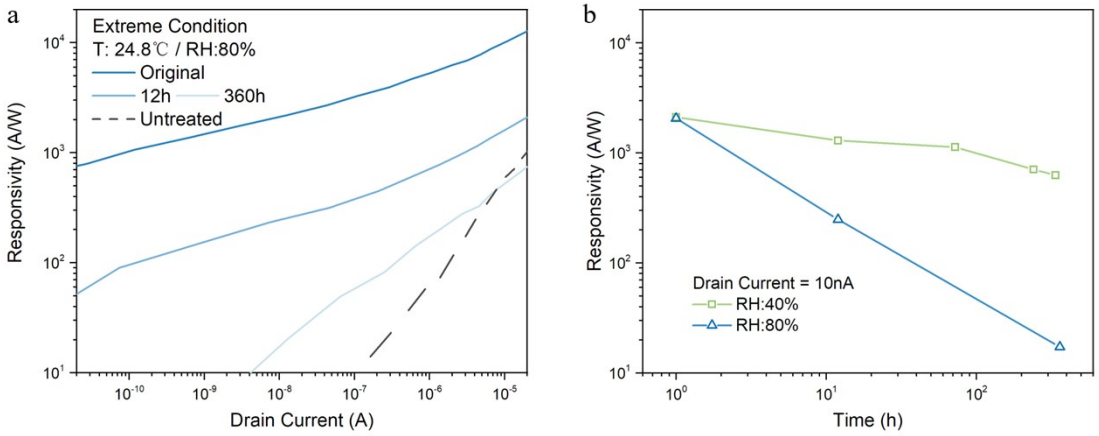

Fig. S12 (a) The variation of photoresponsivity versus drain current curves for the treated PeQD hybrid phototransistor under an extreme condition with RH: 80%. The photoresponsivity of the treated device decreased after 360 hours in this high humidity environment, but could still compete with the original performance of the untreated phototransistor. Here, original performance means that it was measured directly after the untreated device was fabricated. (b) The photoresponsivity lifetime of the AcOEt-treated hybrid phototransistor under conditions with RH: 40% or RH: 80% when transistor drain current is 10 nA.

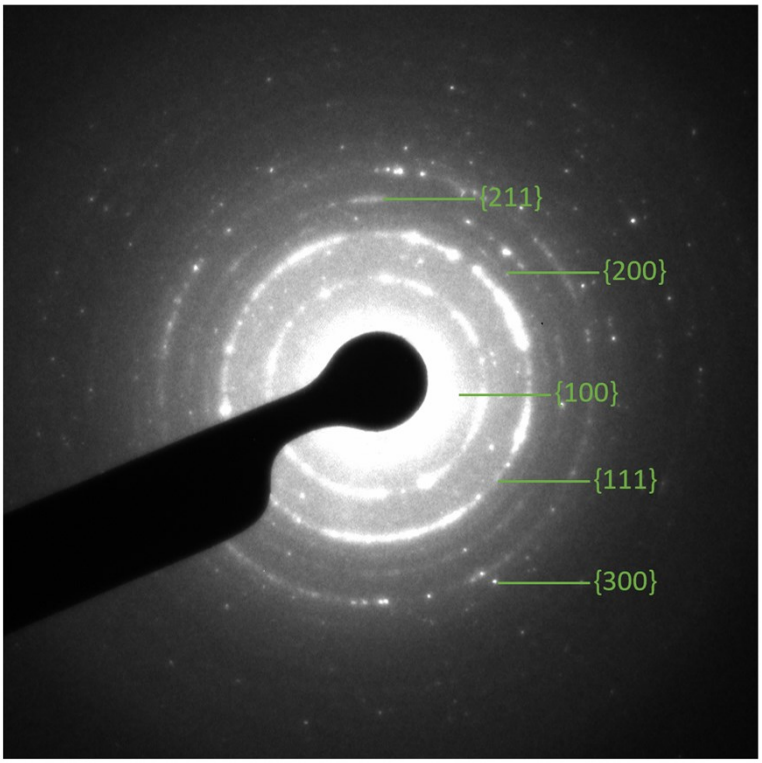

Fig. S13 The electron diffraction pattern of the untreated PeQDs under 300 kV electron beam energy. The facet group marked around patterns are determined according to the crystalline structure data of $CsPbBr_3$ from Inorganic Crystal Structure Database (ICSD=29073).

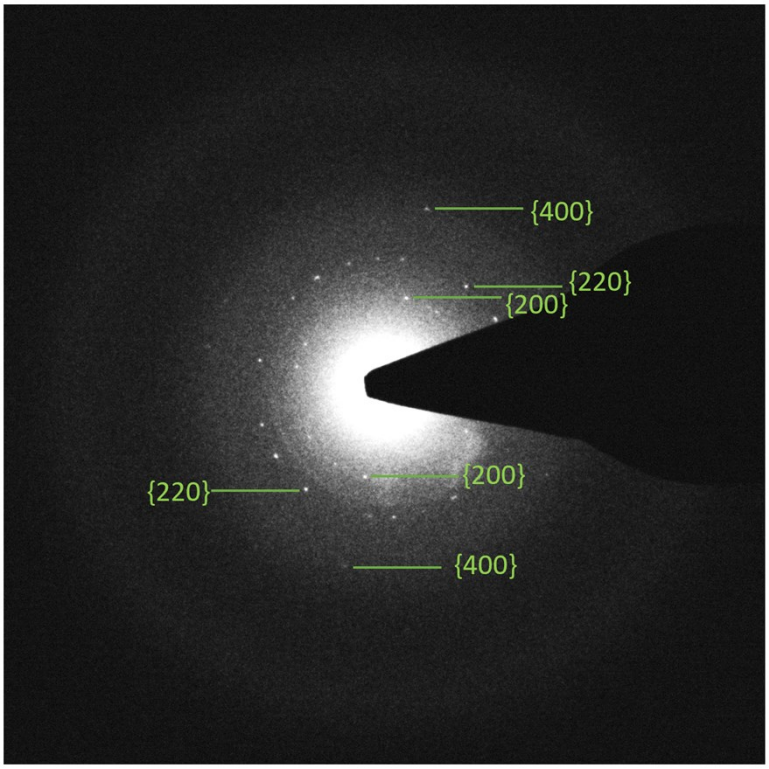

Fig. S14 The electron diffraction pattern of the AcOEt-treated PeQDs under 300 kV electron beam energy. The facet group marked around patterns are determined according to the crystalline structure data of $CsPbBr_3$ from Inorganic Crystal Structure Database (ICSD=29073).

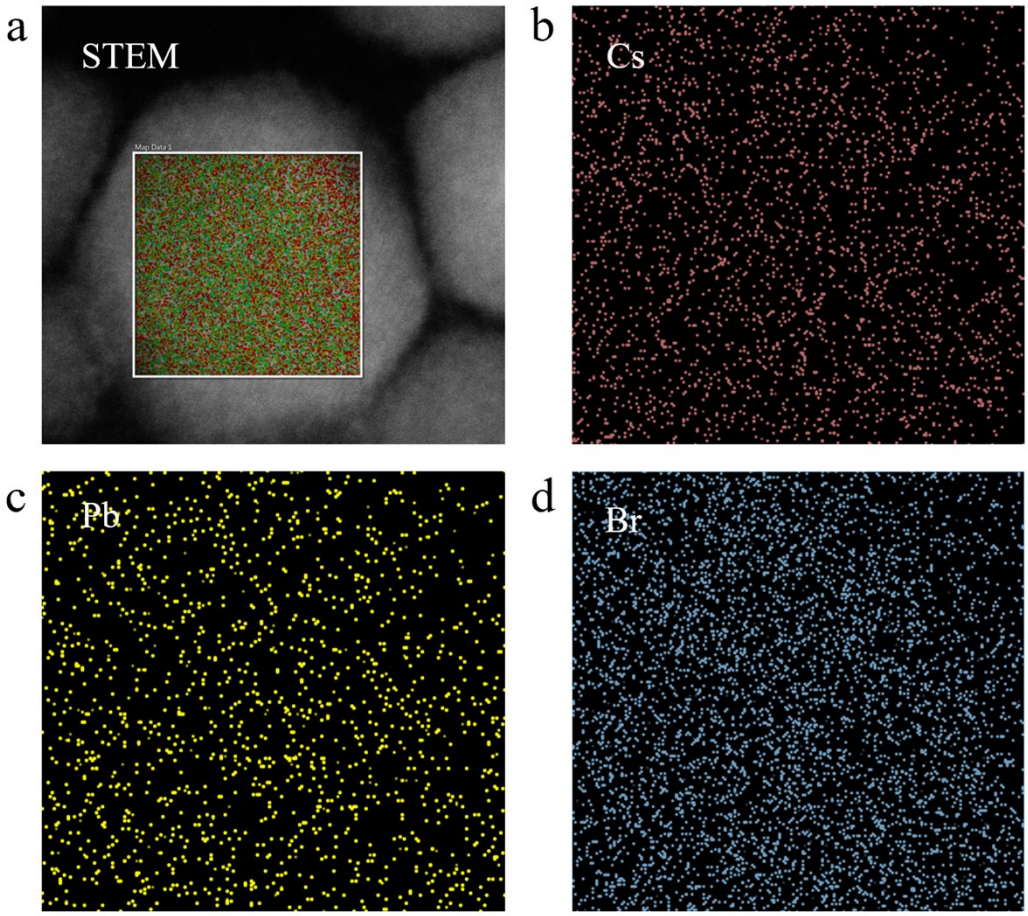

Fig. S15 The EDX mapping of a rectangular region in a STEM image of a treated PeQD. It proves the quantum dot shown in the STEM image to be the PeQD consisting Cs, Pb and Br.

Reference

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