Supplementary Information

PbZrTiO₃ Ferroelectric Oxide as an Electron Extraction Material for Stable Halide Perovskite Solar Cells

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Methods

PZT synthesis. The synthesis of the PZT was done as follows: Zr-isopropoxide $(Zr[OCH(CH_3)_2]_4 - 70 \text{ wt. }\% \text{ in 1-propanol- Sigma)}$ and Ti-isopropoxide $(Ti[OCH-(CH_3)_2]_4 (97\%) \text{ Sigma})$ were mixed and then diluted in acetic acid and n-propanol. Afterwards, Pb acetate (10% excess) [lead(II) acetate trihydrate, Pb(CH_3CO_2)_2•3H_2O (99.999\%)] was dissolved into the above solution heating the solution in a silicon oil bath to 85 °C for dissolving the Pb precursor completely. After the cooling down of the solution, acetic acid and distilled water were added to modify the Pb-Zr-Ti solution and adjust the solution to make 40 ml 0.4 M. The as-prepared solution was used without further modification for spin coating deposition.

Characterization. Absorption spectroscopy measurements were performed with UV-Vis-NIR Spectrophotometer (Cary5, Varian). A high resolution scanning electron microscopy (HR-SEM) was measured by ZEISS Merlin. X-ray diffraction (XRD) of the sample was measured using Empyrean (Panalytical) equipped with a ceramic tube (Cu anode, $\lambda = 1.54060$ Å) and PIXel^{1D} (Panalytical). XRD data were analyzed using HighScore Plus software. High resolution scanning electron microscopy images were obtained by ZEISS Merlin. AFM analyises were carried out with a Nanoscope IV controller and Dimension 3100 head from Veeco.

Device Fabrication. Fluorine doped tin oxide (FTO) substrate (Nippon, 10 Ω /sq) was sequentially sonicated for 15 min in a detergent (2% diluted in DIW, HellmanexIII, Hellma GmbH), DIW, and ethanol. The cleaned FTO glass was exposed to UV/Ozone treatment for 10 min. Once cleaned, 60 µl of PZT solution diluted in acetic acid (1:10 ratio) was spin-coated on

top of the FTO at 4000 rpm with an acceleration of 2000 rpm for 40s. The solution was dried in the hot plate for 5 min at 150° C. The PZT layer was further annealed at 625° C for 10 min in air. The organic cations were purchased from Dyesol; the lead compounds from TCI; CsI from abcr GmbH. The "mixed" perovskite precursor solutions were deposited from a precursor solution containing FAI (1 M), PbI₂ (1.1 M), MABr (0.2 M) and PbBr₂ (0.2 M) in anhydrous DMF:DMSO 4:1 (v:v). We note that this composition contains a lead excess as reported elsewhere.1, 2 Then CsI, predissolved as a 1.5 M stock solution in DMSO, was added to the mixed perovskite precursor to achieve the desired triple cation composition. The prepared perovskite solution was deposited on the PZT substrate (or the SnO₂ reference substrate) using an anti-solvent method. The perovskite solution was spin coated in a two steps program at 1000 and 6000 rpm for 10 and 20 s respectively. During the second step, 100 μ L of chlorobenzene was poured on the spinning substrate 5 s prior to the end of the program. Films with Cs-containing perovskite turned dark immediately after spin coating. The substrates were then annealed (usually at 100 °C) for 1 h in a nitrogen filled glove box. The active area for the devices was 0.16 cm² (masked).

Electrical characterization. The as-prepared solar cells were measured using a 450 W xenon light source (Oriel). The spectral mismatch between AM1.5G and the simulated illumination was reduced by the use of a Schott K113 Tempax filter (Präzisions Glas & Optik GmbH). The light intensity was calibrated with a Si photodiode equipped with an IR-cutoff filter (KG3, Schott), and it was recorded during each measurement. Current-voltage characteristics of the cells were obtained by applying an external voltage bias while measuring the current response with a digital source meter (Keithley 2400). The voltage scan rate was 10 mV s-1 and no device preconditioning, such as light soaking or extended forward voltage biasing in the dark, was applied before starting the measurement. The cells were masked with a black metal mask to fix the active area and avoid artifacts produced by scattered light. The devices for the statistical (champion) measurement was conducted without (with) antireflective coating and on a 0.16 cm2 (0.1225 cm2) mask. The incident light intensity was adjusted to 1000 W/m2 in accordance with standard AM 1.5.

Poling Method. The poling of the cells was performed to the solar cells using a 0.16 cm2 active area mask, using a Keithley 2601 multimeter connected to a computer and software. Poling was carried out at 1 sun A.M. 1.5 G in air (including UV light) without encapsulation through the careful measurement of IV-curves up to 2 V maximum, in reverse mode and applying scan rate of 2 mV/s. IV curves were performed every 5 min until the photovoltaic parameters reached a maximum and stabilized. The reverse IV curves, with a starting voltage 5-10 mV higher than the initial V_{OC} , were iterated until the photovoltaic parameters stabilized. Then, the reverse IV curves were performed with starting voltages successively increasing by 5 - 10 mV until 2 V was reached. Several curves were taken at each starting voltage with varying scan rates (25 - 250 mV/s). Forward and dark-current curves were taken at various points throughout the poling process, and after maximum efficiency had been achieved.

Stability analysis. The stability analyses were carried out at 1 sun AM. 1.5 G (including UV light) in air and without encapsulation applying a sun simulation Steuernagel Solarkonstant KHS1200. Light Intensity was adjusted at 1000 W/m with a bolometric Zipp&Konen CM-4 pyranometer. Calibration of the sun simulator was made by several means, with a calibrated S1227-1010BQ photodiode from Hamamatsu and a mini-spectrophotometer from Ava-Spec 4200. The AM1.5G reference spectrum was according to an ASTMG173 standard. Solar decay and IV-curves were measured using Keithley 2601 multimeter connected to a computer and software. After poling, the PSCs were analysed by consecutive IV curves taken each few minutes in reverse mode with a scan rate of 2 mV/s. The I-V scan starting voltage was established at +1.6 V and the scan final voltage was -0.1 V.

Table S1 – Photovoltaic parameters of the 100 nm PZT (thick) film based PSC, and the reference PSC applying te SnO_2 oxide.

BEFORE POLING						AFTER POLING					
Cell	Scan	j _{sc} (mA/cm²)	V _{oc} (V)	FF (%)	PCE (%)	Cell	Scan	j _{sc} (mA/cm²)	V _{oc} (V)	FF (%)	PCE (%)
100 nm Thick PZT	Forward	0.48	0.51	35.3	0.09	100 nm Thick PZT	Forward	1.12	0.65	37.4	0.27
	Reverse	0.44	0.50	34.8	0.08		Reverse	1.46	0.78	49.9	0.57
Reference SnO ₂	Forward	22.48	1.13	0.78	19.55	Reference SnO ₂	Forward	9.36	1.02	27.3	2.63
	Reverse	22.84	1.12	0.76	19.03		Reverse	2.43	0.94	27.7	0.63



Figure S1 – Characterization of the PZT thin films. a) X-Ray diffraction analysis of the PZT thin film annealed at 625 °C. b-c) Cross-sectional X-TEM mapping, d) Representation of the crystal structure of the PZT.



20/degree



Figure S2. (a) X-Ry diffraction of PZT thin films at different temperatures. (b) The corresponding hysteresis loop of a PZT thin film in a capacitor configuration of the type FTO/PZT/Ag.



Figure S3. Energy-dispersive X-ray spectroscopy (EDX) from a PZT TEM lamella (undiluted). The relative content of Zr:Ti is 0.6:0.4 and therefore the actual stoichiometry of the layer has been determined to be $Pb(Zr_{0.6}Ti_{0.4})O_3$.



Figure S4. Optical properties of the PZT thin film. UV-vis spectroscopy for the PZT electron extraction for (a) different anneal temperatures and (b) for different concentrations (in parts of acetic acid). (c) The PZT is a wide bandgap ferroelectric semiconductor with an optical bandgap of 3.6 eV. (d) the layer thickness can be estimated by the absorbance peak value of the UV-vis spectra.



(b)



Figure S5. Surface roughness and AFM analysis of different PZT thin films obtained at different dilutions during synthesis.

Poling Method. The poling of the cells was performed using a Keithley 2601 multimeter connected to a computer and software. Reverse IV curves with a starting voltage 5-10 mV higher than the initial V_{oc} were iterated until the photovoltaic parameters stabilized. Then, the reverse IV curves were performed with starting voltages successively increasing by 5 - 10 mV until 2 V was reached. Several curves were taken at each starting voltage with varying scan rates (25 - 250 mV/s).



Figure S6. Photovoltaic performance of PSCs of the type: FTO/PZT/CsMAFA/spiro-OMeTAD/Au. I-V curves for the PSC applying the 100 nm thick PZT film (a) as prepared before poling and (b) after 90 min poling in air including UV light (unencapsulated devices). (c) Histogram of the PZT-based PSCs applying the 100 nm thick PZT layer before and after poling. I-V curves for the reference PSC applying SnO₂ (d) before poling and (e) after 90 min poling in air including UV light (unencapsulated devices). (f) Histogram of the reference PSCs applying the SnO₂ electron transport layer.

The photovoltaic response of our PZT-based halide perovskite solar cells are directly influenced by the thickness of the PZT layer. While photovoltaic properties are improved when the PZT thickness decreases from 100 nm to 10 nm, thinner samples (< 10 nm) resulted in the loss of the photovoltaic response, as observed in Figure S6d (for dilutions $c/c_o = 11$ and $c/c_o = 12$). Moreover, poling process for these very thin samples also disappear as the thickness is reduced (Figure S7k and S7l). While it is possible to apply ultrathin compact electron transport layers (ETL) deposited on FTO for perovskite solar cells (PSCs) in either mesoscopic¹ or planar configurations², and ferroelectricity in ferroelectric oxides can still be observed in very thin films below 10 nm³⁻⁷, the response of our solar cells with very thin samples suggests the presence of a different working mechanism. We attribute this response to the presence of pinholes, the possibility of conduction via tunnelling (only observed in a few nanometres thick films^{3,5,8,9}) or the combination of both.



Figure S7. Photovoltaic performance of PZT-based PSC, dependence of PZT dilution during thin film fabrication. Evolution of the solar cell performances (open circuit voltage V_{oc} , short-circuit current j_{sc} , fill factor *FF* and power conversion efficiency *PCE*) as a function of the PZT concentration in parts of acetic acid c/c_0 (i.e. thickness). At least three solar cells were fabricated for each condition. The condition BP on fresh ferroelectric/perovskite solar cells was after a forward I-V scan from [-0.1 V - 1.1 V]. The condition AP is after the poling process as described in the main text. BP: *before poling*, AP: *after poling*.



Figure S8. Evolution of IV curves of the PZT-based PSC during poling under UV light. A representative I-V after the poling processes for each PZT dilution: (a) 1:1, (b) 1.2, (c) 1:3, (d) 1:4, (e) 1:5, (f) 1:6, (g) 1:7, (h) 1:8, (i) 1:9, (j) 1:10 and (k) 1:11, (l) 1:12. The photovoltaic current progressively increases as the ferroelectric PZT layer thickness is reduced with a turning point around 1:4. Then, the j_{sc} slightly increases up to 1:10 which is condition exhibiting the largest PCE. For thinner PZT layers it has been found to be challenging in practice to perform the full poling procedure without breakdown phenomena as shown for 1:11.

IPCE. Figure S8 shows the IV curve and the corresponding IPCE analysis of the PZT-based PSC applying the thin (100 nm) PZT layer (a and b) and the corresponding graphs for the reference PSC made with the SnO₂ electron transport layer (c and d). IPCE spectra of the PZT-based PSCs were difficult to perform without light irradiation. Once the device is in the dark the IPCE value show negligible values. This is probably due to the PZT layer, which returns to its original insulating (non-conducting) state when standing without poling field in the dark²³. Thus, the IPCE spectra shown in Figure S8a corresponds to a device that was maintained under light irradiation for several minutes before the IPCE spectra was measured (See also Figure S9).



Figure S9. IV curves and IPCE spectra, including the integrated response, for a PZT-based PSC (a-b) and for a reference solar cell applying the SnO_2 as electron transport layer (c-d).

Transport properties and the enhancement of remnant polarization (Figure S9). To analyse the evolution of the transport properties of the PZT-based PSC under UV light and poling, we carried out experiments of IPCE (or EQE) against poling time. We then compared the J_{sc} obtained from the IPCE and the one obtained from the IV curves at specific times. The poling experiments were carried out at 0.1 h, 1.0 h, 2.5 h and 5 h following the same poling procedure described in the manuscript (under the sun simulator, up to 2 V). After each poling period the sample was taken out of the sun simulator and immediately analysed by IPCE. Figure S9 shows the IPCE (Figure S9a) and the normalized IPCE (Figure S9b) after 0.1 h, 1.0 h, 2.5 h and 5.0 h (labelled 1 to 4 respectively).

The first observation is that by increasing the poling time from 0.1 h to 5 h, the conversion of photons to electrons increases from 4 % to 60 %. Since the PZT is originally an insulator, very low charge transport is initially observed (Figure S9 a-1). As the irradiation under UV light and poling increases the PZT increases its transport properties and the overall IPCE improves. The transformation of the PZT with time and the improvement of IPCE (and solar cell efficiency) can also be explained by the shape of the IPCE spectra. Figure S9b shows the normalized IPCE. The initial spectra obtained after 0.1 h of poling (1) revealed a very weak adsorption (about 4% IPCE, Figure S9a) of the PZT oxide at wavelengths below 400 nm, at 340 nm, corresponding with a very poor semiconductor. At this time, no adsorption of the halide perovskite (CsMAFA) between 400 -800 nm, is observed since no current flow can take place (2). As the poling under UV light continues this peak, at 340 nm, red shifts to 380 nm (from 3.64 to 3.26 eV). A reduction of the band gap of oxides is commonly observed during oxide doping [e.g. in TiO₂ ^{10,11}, PZT ¹²], and also due to the continuous and steady removal of O_{vac} under UV light exposure or inert atmospheres (^{13,14}. Gradually, the increase of the poling time, from 0.1 h to 1.0 h and 2.5 h, results in the improvement of the IPCE absorption between 400 nm and 800 nm, which is the region that corresponds to the halide perovskite (CsMAFA), Figure S9b. This is an indication of charge transport throughout the PSC. We should also emphasize that the shape of the IPCE obtained after 5 h poling (4) corresponds exactly with the shape of the IPCE of a PSC applying the classical SnO₂ oxide as ETL¹⁵.

Finally, we compare the response observed for the current density (I_{sc}) obtained from IV curves and IPCE after poling (Figure S9c). In both cases, the J_{sc} shows a steadily increases until both J_{sc} reach a similar value around ~ 14 mA/cm² after the 5 h poling process. We observed however, that for the intermediate poling times between 0.1 h, 1.0 h and 2.5 h, the J_{sc} obtained from IPCE is always lower than the J_{sc} obtained from the IV curves (Figure S9c). The main difference between both characterization methods is that IV curves are carried out under full illumination (including UV light) under the sun simulator, right after poling. In the case of the IPCE characterization, illumination and poling are eliminated once the samples are taken out of the sun simulator and placed under the IPCE set up for analysis. Thus, the removal of UV light and poling in PZT samples brings the material back to its original state: electrostatic repulsion between polarization charges and defect charges (O_{vac}) immediate occurs¹⁶ and the depolarization of the film is observed. Since remnant polarization is defined as the polarization remaining in the material after the poling voltage is reduced to zero, the J_{sc} observed from the IPCE is probably linked to the remnant polarization since it is obtained without poling. We also observed a relationship between poling time and current density: the longer the poling time under UV, the larger the J_{sc} (and the remnant polarization), until reaching saturation after 5 h of poling (4). The latter is in perfect agreement with the mechanism reported by Cao, et al ¹⁶.



Figure S10. IPCE analysis and J_{sc} **during poling.** (a) IPCE and (b) normalized IPCE observed during poling and UV light irradiation of a PZT-based PSC at different times. (c) Comparison of current density (J_{sc}) obtained from IPCE spectra (squares) and IV curves (circles). IV curves were measures under the sun simulator (1 sun) including UV light and poling. IPCE were carried out after poling and after taking the sample out of the sun simulator. Numbers 1 to 4 represent poling times: 1) 0.1 h, 2) 1.0 h, 3) 2.5 h and 4) 5.0 h.



Figure S11. Evolution of the photovoltaic parametres of the PSC before poling (open símbols) and after poling (full symbols) applying the 30 nm thin PZT layer (red) and the reference SnO_2 oxide (blue).

Remnant polarization and the presence of Pb³ (Figure S11). In FE-Oxides, UV light can photoinduce the enhancement of the remnant polarization, as recently reported for $PbZrTiO_3$ (PZT) films¹⁶. Giant enhancement of ferroelectric polarization under UV illumination has also been reported for Li^{1+} and Bi^{3+} doped PZT ¹⁷. In these examples, the Pb^{2+} site in the perovskite PZT lattice acts as hole traps resulting in metastable Pb^{3+} centers. After poling, the photo-generated charges accumulate in the ferroelectric domains, locking them by carrier injection. Thus, the presence of Pb^{3+} on the PZT films after UV light illumination and poling could explain the enhancement of the remnant polarization. To prove the later, we carried out x-ray photoelectron spectroscopy (XPS) experiments to PZT samples deposited on Glass/FTO substrates.

The XPS experiment set-up is shown in Figure. S11a. The UVA-LED source is a commercial UVA LED from Roithner part APG2C1-365-E 1W 365 nm. The nominal 365 nm UVA-LED irradiation peak was centred at 369.2 nm with a FWHM of 9.6 nm (Figure S11b). In one experiment, the sample was illuminated thought the Glass/FTO side, as in a PSC (UV1). To improve XPS response, a second sample was illuminated directly on the PZT samples (UV2). The irradiance at the top PZT surface is approximately $\sim 3 \text{ mW/cm}^2$ for the samples illuminated from the Glass/FTO side, while the irradiance at the PZT surface in the configuration UV2 is ~15 mW/cm². Both samples were illuminated for several hours in air condition but shielding the devices from additional natural light. After the UV-illumination test, samples were immediately mounted into the XPS chamber and a normal scan was then performed. A comparison of the XPS scans reveal structural changes in the PZT surface composition after UV illumination as shown in Figure R9(c) and (d). The shoulders of the UV-irradiated Pb 4f signal are notable. The XPS Pb 4f signal can be well reproduced with contributions from perovskite Pb^{2+} (PbO) and $\sim Pb^{3+}$ (i.e., Pb_3O_4). This result agrees with the report of Robertson and coworkers ¹⁸ where the Pb^{3+} centres are revealed by electron paramagnetic resonance after UV-optical illumination and are found to be metastable at room temperature. The Pb³⁺ centre was reported to be a hole trapped at a Pb^{2+} site in the PZT perovskite lattice. When poled, these ionized centres first pin the surface polarization. Afterwards, the photo-generated charges accumulate in the ferroelectric domains, locking them by carrier injection. This is therefore a plausible origin of the enhancement of the remnant polarization.



Figure S12. The presence of Pb³⁺. (a) X-ray photoelectron spectroscopy (XPS) additional experiment setup to confirm the charge accumulation at the ferroelectric oxide surface which enables the enhancement of the remnant polarization after poling. (b) Comparison of the characteristic UV-LED spectra with respect to a standard natural illumination lab light (white LED) and the typical solar simulator spectra. (c) The UV-illumination results in sizable oxidation state changes as revealed by the XPS scans. (d) In particular, the Pb 4*f* scan suggests hole accumulation at the surface after UV-light irradiation.

Photoactivity of PZT films (Figure S12). Another characteristic of the PZT working as ETL in PSCs, is its lower photoactivity under UV light, which results in enhanced stability when applied in solar cells. Cao, et al. stated that in PZT O_{vac} (defect charges), responsible of charge separation and current transport, are removed after poling under UV light. This suggests a different working mechanism than the observed for classical oxides like SnO₂ or TiO₂ where O_{vac} act as photoreactive sites.

To prove the later, we carried out a photocatalyst experiment where a thin film of P3HT/PCBM was deposited by spin coating on top of three samples: bare FTO, TiO_2 and PZT. All samples were exposed to the same conditions used for stability analysis of the PSCs: 1 sun (including UV light), without encapsulation, in ambient air, ~ 50 %RH. All samples were left at the same time under the sun simulator for a period of 10 h. UV-VIS analyses were carried out on the thin films every hour until the analysis was completed. After each UV analysis the samples were re-exposed to the 1 sun irradiation of the sun simulator.

Figure S12 shows the UV-VIS absorption spectra of the three samples after the 10-hour analysis. The absorption range for the P3HT:PCBM thin film is observed within the visible region, between 400 and 600 nm (Fig S12a). During degradation studies on FTO, its adsorption spectra show minimal differences around 550 nm but in general the adsorption peaks are maintained almost unchanged. Figures S12b and S12c show the degradation of the P3HT:PCBM on top of the TiO₂ and the PZT, respectively. In both cases the absorption region between 400-600 nm decreases with time. In the case of the TiO₂ the degradation is slowly and steady since the beginning of the study, in correspondence with the behaviour of a very good photocatalyst, as expected. However, in the case of the PZT (Figure S12c), the P3HT:PCBM region is maintained unaffected for several hours. Even after 7 h the spectra is maintained unaffected. Is after 8 h when degradation of the P3HT:PCBM is observed. The latter is a clear indication that the photodegradation mechanisms of the PZT, especially for the initial hours of analysis.



Figure. S13. A photodegradation study. UV vis analysis of a P3HT:PCBM thin film layer at different degradation times (in air, 1 sun including UV light) on top of different substrates: a) FTO (as reference), b) TiO₂ and c) PZT.



Figure S14. Hysteresis. Analysis of the hysteresis index (HI) as a function of (a) the poling state and (b) during the poling process for a forward and reverse scan.

Polarity inversion. A bias polarity inversion (negative poling) has a detrimental effect on the photovoltaic performances, in particular, the photovoltaic current. Therefore, the negative poling effect results in a significant reduction of the power conversion efficiency of the device. To analyse the effect of the negative bias polarity, we have applied three subsequent different poling processes (labelled as A, B and C in Figure S14) to our PZT-based PSCs.



Figure S15. Effect of negative bias poling. Evolution of the photovoltaic parameters of a PZT-based PSC under positive and negative bias poling processes. (A) main poling, (B) poling inversion under constant bias voltage and (C) poling inversion under increasing bias voltage.

Poling Section A (main poling). This method is the standard poling process described in the main text. During this poling, reverse IV curves, with a starting voltage 5-10 mV higher than the initial V_{oc} and a final voltage of -0.1 V, were iterated until the photovoltaic parameters were stabilized. Then, the reverse IV curves were performed with starting voltages successively increased by 5 - 10 mV until an optimal initial reverse voltage bias for the scan was established (the typical value was +1.6-1.8 V). The reference scan rate for this experiment is 50 mV/s. In short, [-0.1,1.1+ Δ V]; Δ V= 10 mV, V_{max} =+1.8V, scan rate = 50 mV/s.

Poling Section B (poling inversion at constant voltage). Once the PCE was stabilized in an optimum point, the reverse starting poling voltage was kept fixed and then the minimum voltage bias was progressively increased by a factor of ΔV = 10 mV until the initial and the final voltage bias of the reverse scan is the same. In short, [-0.1- ΔV , V_{max}]; ΔV = 10 mV, V_{min} =- V_{max} , scan rate = 50 mV/s.

Poling Section C (poling inversion at increasing voltage). In the last section of the poling, the minimum voltage of the scan is progressively increased and therefore overpasses in absolute value to the positive bias poling. In short, $[-V_{max}-\Delta V, V_{max}]$; $\Delta V = 10 \text{ mV}$, scan rate = 50 mV/s.

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