Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Mechanism of Biphasic Charge Recombination and Accumulation in TiO_2 Mesoporous Structured Perovskite Solar Cells

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Experimental section

First of all, fluorine doped tin oxide glasses (FTO, Pilkington TEC-7, 7 Ω/sq) were pre-patterned by etching with Zn powder and diluted HCl. Then the substrates were successively rinsed with detergent, deionized water, acetone and ethanol using an ultrasonic bath for 15 min, respectively. After drying under compressed N_2, the substrates were subjected to an ultraviolet plasma treatment for 20 min to get rid of organic residues. A thin compact layer of TiO_2 was deposited on the pre-cleaned FTO plates by spin-coating a titanium diisopropoxide bis(acetylacetonate) solution (75% in isopropyl alcohol (IPA)) diluted in n-butyl alcohol (2:25 v/v) followed by 15 min thermal treatment. Afterwards, a diluted commercial TiO_2 paste was spin-coated on the top of the compact layer. The films were then sintered at 500 ºC for 30 min.

The active layer manipulation process is similar with the so-called modified sequential deposition as pre-reported. Briefly, the mesoporous TiO_2 films were

infiltrated by 20 µL of PbI_2 solution (1 M in DMF) prior to spin-coating at 4000 rpm, then the films were dried at 70 °C. While cooling to room temperature, 200 µL of methylammonium iodide (MAI) solution in IPA with certain concentrations was dropped on the top of the PbI_2 film. Then the films were spun at 4000 rpm for 20 s to spread out the excess MAI solution. Thereafter the films were annealed at 100 °C for 30 min to constitute perovskite crystal. The hole transport material (HTM) was subsequently deposited by spin-coating the precursor solution at 1000 rpm for 5s and 4000 rpm for 20s. The HTM recipe was prepared by dissolving 72.3 mg of 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9-spirobifluorene, 28.8 µL of 4-tert-butylpyridine, 17.5 µL of a stock solution of 520 mg/mL lithium bis(trifluoromethylsulphonyl)imide in acetonitrile and 29 µL of a stock solution of 300 mg/mL tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)cobalt(III) bis(trifluoromethylsulphonyl)imide in acetonitrile in 1 mL of chlorobenzene. Finally, 60 nm of Au was thermally evaporated as the electrode. The device fabrication was carried out in an inert glove-box. Herein, three target sample devices fabricated from the different MAI solution concentrations of 8 mg/mL, 12 mg/mL and 14 mg/mL are named Cell-L, Cell-M and Cell-S, respectively, corresponding to the resulting large, middle and small perovskite particle sizes.

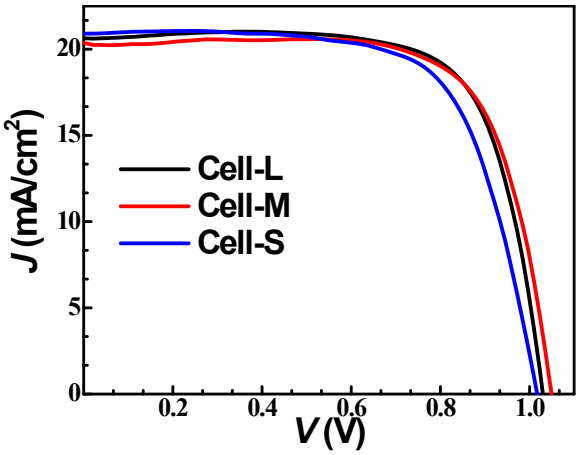

Fig. S1 Sample *J*-*V* curves of relevant devices mostly approaching the average performances.

Table S1 Photovoltaic parameters of relevant devices mostly approaching the average performances

	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
Cell-L	20.62	1.030	0.73	15.46
Cell-M	20.35	1.049	0.72	15.37
Cell-S	20.89	1.017	0.68	14.52

Table S2 Photovoltaic performance parameters for statistical analysis of device named Cell-L

Sample No. (Cell-L)	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	PCE (%)
1	21.90	1.073	0.75	17.57
2	21.81	1.042	0.74	16.96
3	21.58	1.026	0.75	16.55
4	21.48	1.029	0.72	16.01
5	20.61	1.045	0.74	15.89
6	20.51	1.067	0.72	15.88
7	21.83	1.031	0.70	15.84
8	21.57	1.073	0.68	15.80
9	20.62	1.030	0.73	15.46
10	20.08	1.002	0.74	14.87
11	21.08	1.004	0.69	14.73
12	21.07	1.034	0.67	14.64
13	19.92	0.985	0.74	14.50
14	21.16	1.028	0.65	14.22
15	20.47	0.977	0.66	13.24
Mean	**21.05**	**1.030**	**0.71**	**15.48**
STDEV	**0.65**	**0.029**	**0.03**	**1.13**

Table S3 Photovoltaic performance parameters for statistical analysis of device named Cell-M

Sample No. (Cell-M)	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	PCE (%)
1	21.45	1.031	0.72	15.90
2	20.49	1.068	0.73	15.89
3	20.10	1.069	0.74	15.83
4	21.23	1.044	0.71	15.65
5	19.94	1.071	0.73	15.60
6	20.11	1.074	0.72	15.53
7	20.30	1.062	0.72	15.48
8	20.35	1.049	0.72	15.37
9	20.12	1.041	0.73	15.33
10	19.81	1.048	0.73	15.23
11	19.78	1.033	0.74	15.09
12	19.75	1.047	0.73	15.07
13	20.39	1.036	0.71	14.93
14	20.65	1.051	0.69	14.92
15	19.41	1.053	0.73	14.86
Mean	**20.26**	**1.052**	**0.72**	**15.38**
STDEV	**0.55**	**0.014**	**0.01**	**0.36**

Table S4 Photovoltaic performance parameters for statistical analysis of device named Cell-S

Sample No. (Cell-S)	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	PCE (%)
1	21.23	1.025	0.72	15.58
2	21.28	1.023	0.70	15.26
3	19.90	1.027	0.74	15.19
4	20.00	1.042	0.73	15.16
5	19.61	1.056	0.73	15.15
6	20.89	1.017	0.68	14.52
7	19.66	1.028	0.70	14.15
8	19.43	1.036	0.70	13.99
9	20.64	1.041	0.65	13.89
10	20.16	0.985	0.65	12.85
Mean	**20.28**	**1.028**	**0.70**	**14.57**
STDEV	**0.68**	**0.019**	**0.03**	**0.85**

Table S5 Parameters of bi-exponential fitting for TPV decay trace (Cell-L)

V_{ph} （mV）	V_{base}	A_1	τ_1 (s)	A_2	τ_2 (s)	τ_n (s)
56	0.04	0.693	6.86E-03	0.443	3.00E-03	5.35E-03
79	0.04	0.616	3.30E-03	0.464	2.44E-03	2.93E-03
104	0.04	0.626	3.63E-03	0.449	2.49E-03	3.15E-03
124	0.05	0.734	7.88E-04	0.231	6.30E-03	2.11E-03
149	0.05	0.780	1.16E-03	0.244	8.23E-03	2.85E-03
175	0.05	0.714	3.90E-03	0.401	2.99E-03	3.57E-03
196	0.05	0.680	4.71E-03	0.412	3.10E-03	4.10E-03
225	0.04	0.567	2.31E-03	0.417	2.25E-03	2.28E-03
248	0.05	0.729	1.10E-03	0.297	7.05E-03	2.82E-03
281	0.04	0.816	9.28E-04	0.224	6.97E-03	2.23E-03
298	0.05	0.784	7.96E-04	0.231	6.65E-03	2.13E-03
318	0.05	0.798	1.09E-03	0.240	7.92E-03	2.67E-03
348	0.04	0.811	9.59E-04	0.216	7.99E-03	2.44E-03
387	0.04	0.795	7.37E-04	0.218	6.27E-03	1.93E-03
407	0.04	0.835	8.44E-04	0.200	7.86E-03	2.20E-03
426	0.05	0.792	8.47E-04	0.236	6.56E-03	2.16E-03
449	0.03	0.867	6.27E-04	0.244	4.94E-03	1.57E-03
467	0.03	0.827	6.15E-04	0.193	4.84E-03	1.41E-03
498	0.03	0.766	5.07E-04	0.216	4.87E-03	1.47E-03
523	0.03	0.814	4.41E-04	0.206	4.61E-03	1.28E-03
545	0.04	0.805	5.70E-04	0.243	6.52E-03	1.95E-03
576	0.03	0.748	9.28E-04	0.289	1.05E-03	9.62E-04
606	0.03	0.702	8.07E-04	0.388	5.69E-04	7.22E-04
622	0.03	0.754	6.74E-04	0.328	6.13E-04	6.56E-04
652	0.03	0.763	8.39E-04	0.301	8.42E-04	8.40E-04
681	0.03	0.804	8.18E-04	0.266	9.26E-04	8.45E-04
705	0.02	0.749	6.64E-04	0.338	4.84E-04	6.08E-04
726	0.02	0.796	4.70E-04	0.305	6.66E-04	5.24E-04
751	0.02	0.828	4.04E-04	0.292	5.69E-04	4.47E-04
781	0.02	0.841	3.83E-04	0.295	5.23E-04	4.20E-04
805	0.02	0.639	1.88E-04	0.389	1.45E-04	1.71E-04
828	0.02	0.731	1.71E-04	0.322	1.84E-04	1.75E-04
849	0.01	0.692	1.05E-04	0.365	1.18E-04	1.09E-04
882	0.01	0.759	4.99E-05	0.335	9.36E-06	3.75E-05
909	0.02	0.616	5.03E-05	0.458	1.14E-05	3.37E-05

Table S6 Parameters of bi-exponential fitting for TPV decay trace (Cell-M)

V_{ph} (mV)	V_{base}	A_1	τ_1 (s)	A_2	τ_2 (s)	τ_n (s)
53	0.02	0.975	1.33E-03	0.111	1.25E-02	2.48E-03
74	0.03	0.943	1.33E-03	0.117	9.38E-03	2.22E-03
101	0.02	1.009	1.53E-03	0.086	1.94E-02	2.93E-03
129	0.03	0.788	8.26E-04	0.287	3.74E-03	1.60E-03
149	0.03	0.828	7.95E-04	0.239	3.93E-03	1.50E-03
171	0.03	0.839	7.28E-04	0.242	3.66E-03	1.38E-03
196	0.03	0.851	9.69E-04	0.226	4.31E-03	1.67E-03
225	0.03	0.895	7.15E-04	0.198	4.30E-03	1.36E-03
251	0.03	0.744	6.73E-04	0.359	2.87E-03	1.39E-03
279	0.04	0.764	4.62E-04	0.389	2.42E-03	1.12E-03
294	0.03	0.890	6.51E-04	0.214	3.61E-03	1.23E-03
328	0.03	0.797	5.51E-04	0.223	2.41E-03	9.58E-04
359	0.05	0.808	5.39E-04	0.339	2.41E-03	1.09E-03
380	0.04	0.730	5.33E-04	0.380	2.14E-03	1.08E-03
396	0.04	0.779	6.30E-04	0.267	2.58E-03	1.13E-03
419	0.04	0.900	7.38E-04	0.228	3.28E-03	1.25E-03
439	0.03	0.702	5.78E-04	0.293	2.47E-03	1.14E-03
480	0.03	0.654	3.35E-04	0.356	1.66E-03	8.02E-04
507	0.03	0.746	5.16E-04	0.299	2.25E-03	1.01E-03
532	0.02	0.636	4.27E-04	0.346	1.77E-03	9.00E-04
550	0.03	0.738	4.02E-04	0.299	2.02E-03	8.69E-04
575	0.03	0.769	5.04E-04	0.273	2.23E-03	9.55E-04
600	0.02	0.747	6.73E-04	0.289	1.82E-03	9.93E-04
624	0.02	0.659	1.17E-03	0.406	5.15E-04	9.23E-04
656	0.02	0.631	1.05E-03	0.412	1.52E-04	6.95E-04
677	0.02	0.698	6.50E-04	0.370	9.53E-04	7.55E-04
700	0.02	1.012	3.66E-04	0.248	1.92E-03	6.72E-04
723	0.02	0.800	8.00E-04	0.461	3.68E-04	6.42E-04
752	0.02	0.976	4.32E-04	0.133	2.07E-03	6.29E-04
778	0.01	1.168	3.85E-04	0.185	1.03E-03	4.73E-04
799	0.01	0.596	6.07E-04	0.428	2.63E-04	4.63E-04
823	0.01	0.834	3.57E-04	0.155	4.04E-04	3.64E-04
849	0.02	0.892	1.73E-04	0.111	1.13E-03	2.79E-04
874	0.01	0.881	1.16E-04	0.117	5.77E-04	1.70E-04
900	0.01	0.926	1.00E-04	0.108	5.38E-04	1.46E-04

Table S7 Parameters of bi-exponential fitting for TPV decay trace (Cell-S)

V_{ph} (mV)	V_{base}	A_1	τ_1 (s)	A_2	τ_2 (s)	τ_n (s)
26	0.01	0.787	8.17E-04	0.295	5.06E-03	1.98E-03
52	0.01	0.799	6.83E-04	0.231	3.88E-03	1.40E-03
73	0.02	0.729	7.28E-04	0.286	4.39E-03	1.76E-03
100	0.02	0.758	4.92E-04	0.246	4.04E-03	1.36E-03
120	0.03	0.691	4.24E-04	0.276	3.30E-03	1.24E-03
147	0.03	0.720	5.09E-04	0.252	4.23E-03	1.48E-03
181	0.03	0.744	4.66E-04	0.254	3.72E-03	1.29E-03
200	0.03	0.743	7.73E-04	0.276	5.09E-03	1.94E-03
231	0.03	0.726	4.12E-04	0.300	3.67E-03	1.36E-03
245	0.03	0.707	3.08E-04	0.294	3.26E-03	1.18E-03
263	0.03	0.722	3.86E-04	0.266	3.52E-03	1.23E-03
295	0.04	0.662	5.58E-04	0.333	4.30E-03	1.81E-03
330	0.03	0.735	3.46E-04	0.271	3.53E-03	1.20E-03
351	0.03	0.721	4.59E-04	0.294	3.86E-03	1.44E-03
379	0.03	0.735	4.88E-04	0.286	3.99E-03	1.47E-03
393	0.03	0.709	4.95E-04	0.347	3.48E-03	1.48E-03
422	0.03	0.732	7.23E-04	0.291	4.47E-03	1.79E-03
453	0.02	0.745	3.48E-04	0.298	2.48E-03	9.58E-04
469	0.03	0.706	4.64E-04	0.310	3.12E-03	1.27E-03
501	0.03	0.764	4.80E-04	0.277	2.96E-03	1.14E-03
528	0.03	0.745	2.64E-04	0.317	2.17E-03	8.33E-04
549	0.03	0.669	2.54E-04	0.327	2.04E-03	8.41E-04
585	0.03	0.680	2.52E-04	0.329	2.01E-03	8.25E-04
599	0.02	0.648	2.33E-04	0.342	1.73E-03	7.50E-04
615	0.02	0.684	2.31E-04	0.321	1.68E-03	6.94E-04
645	0.02	0.700	1.71E-04	0.313	1.40E-03	5.51E-04
671	0.02	0.695	2.22E-04	0.320	1.43E-03	6.03E-04
696	0.02	0.759	1.93E-04	0.273	1.38E-03	5.07E-04
717	0.02	0.783	2.84E-04	0.257	1.74E-03	6.44E-04
754	0.02	0.793	2.11E-04	0.261	1.16E-03	4.46E-04
774	0.02	0.731	1.83E-04	0.324	9.81E-04	4.28E-04
798	0.01	0.745	1.21E-04	0.297	7.13E-04	2.90E-04
821	0.01	0.734	1.37E-04	0.303	6.82E-04	2.96E-04
853	0.01	0.764	7.57E-05	0.288	4.74E-04	1.85E-04
878	0.01	0.628	3.81E-05	0.353	2.43E-04	1.12E-04
904	0.01	0.699	3.93E-05	0.318	2.47E-04	1.04E-04
934	0.01	0.707	2.51E-05	0.312	1.55E-04	6.50E-05
951	0.01	0.710	1.87E-05	0.314	1.17E-04	4.90E-05
975	0.01	0.764	1.46E-05	0.289	8.69E-05	3.45E-05
999	0.00	0.865	1.22E-05	0.228	7.53E-05	2.53E-05

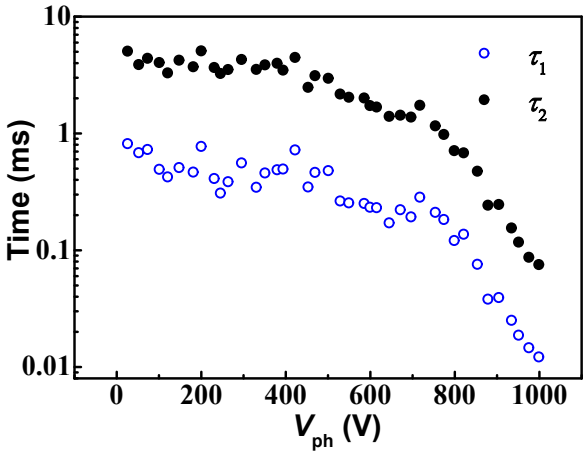

Fig. S2 Fitting parameters τ_1 and τ_2 of Cell-S, which show similar dependency on V_{ph}.

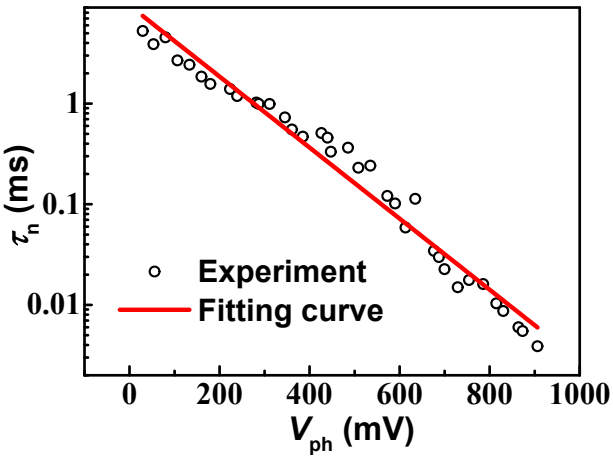

Fig. S3 Charge carrier lifetimes extracted from TPV measurement of planar configuration device without mesoporous TiO_2.

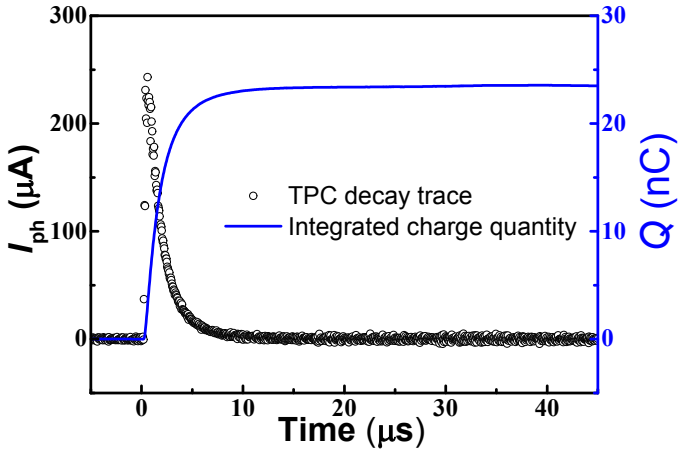

Fig. S4 Sample TPC decay trace and integrated charge amount.

Transient photocurrent measurement was conducted for calculation of capacitance parameters. It was recorded by immediately switching the oscilloscope

input impendence to 50 Ω after TPV data were recorded.

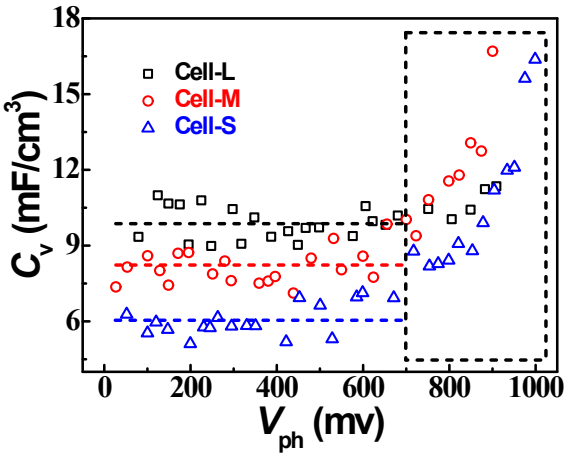

Fig. S5 Calibrated efficient capacitance in unit volume.

The efficient capacitance in unit volume (C_v) is calibrated following the equation bellow to eliminate the effect of film thickness and porosity.

$$C_v = \frac{\Delta Q}{ds(1-p)\Delta V}$$

ΔQ is extracted by integration of the intrinsic TPC signal (Fig. S3 shows example TPC trace and integration result) and ΔV is the amplitude of relative TPV signal, d is the average film thickness of perovskite/meso-TiO_2 layer obtained from cross-section SEM images, p is the volume porosity acquired by gray analysis of the top-view SEM images,[1] and the active area s is set to be 0.1 cm^2.

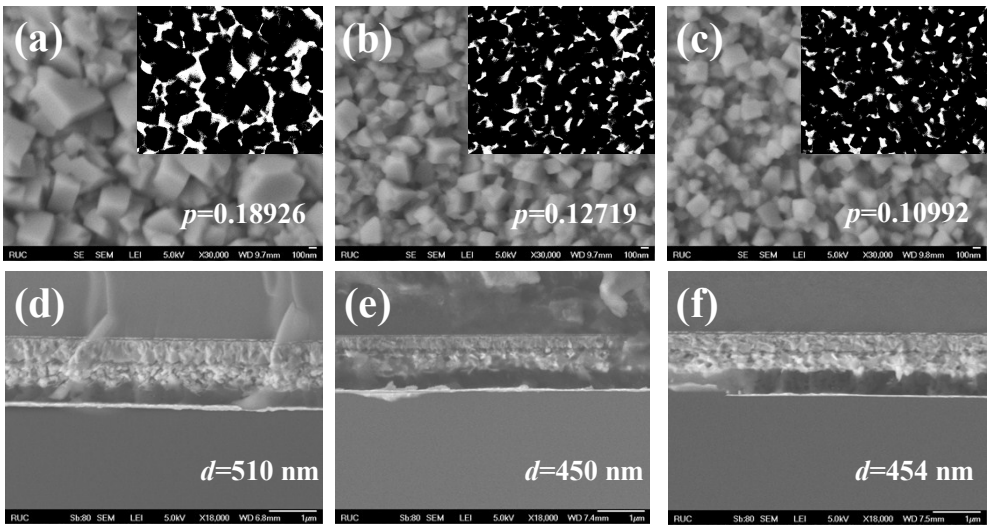

Fig. S6 Top-view and cross-section SEM images of relevant devices. Insets show the gray analysis examples. (a) (d), (b) (e) and (c) (f) corresponds to Cell-L, Cell-M and Cell-S.

Reference

(1) Okabe, H.; Blunt, M. J., *Phys. Rev. E*, 2004, **70**, 066135.