Supplementary Materials

Use of carbon electrodes to reduce mobile ion concentration and improve reliability of metal halide perovskite photovoltaics

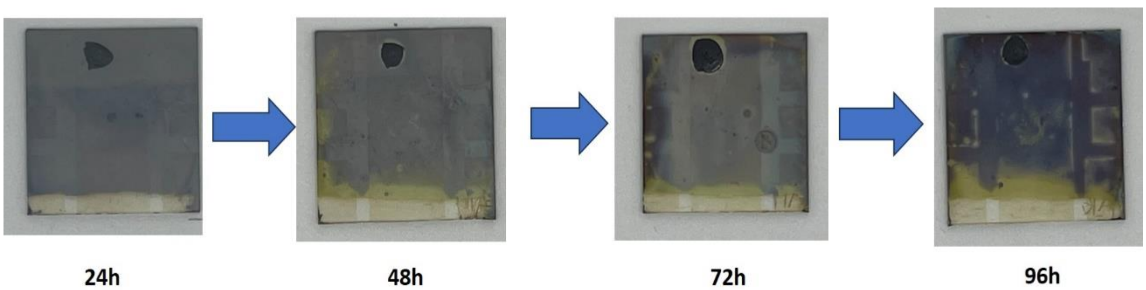
Saivineeth Penukula[1], Favian Tippin[1], Muzhi Li[1], Kausar Ali Khawaja[2], Feng Yan[2], Nicholas Rolston[1,*]

[1]Renewable Energy Materials and Devices Lab, School of Electrical, Computer and Energy Engineering (ECEE), Arizona State University, Tempe, AZ 85284, USA.
[2]School for Engineering of Matter, Transport and Energy, Arizona State University, Tempe, AZ 85281, USA.

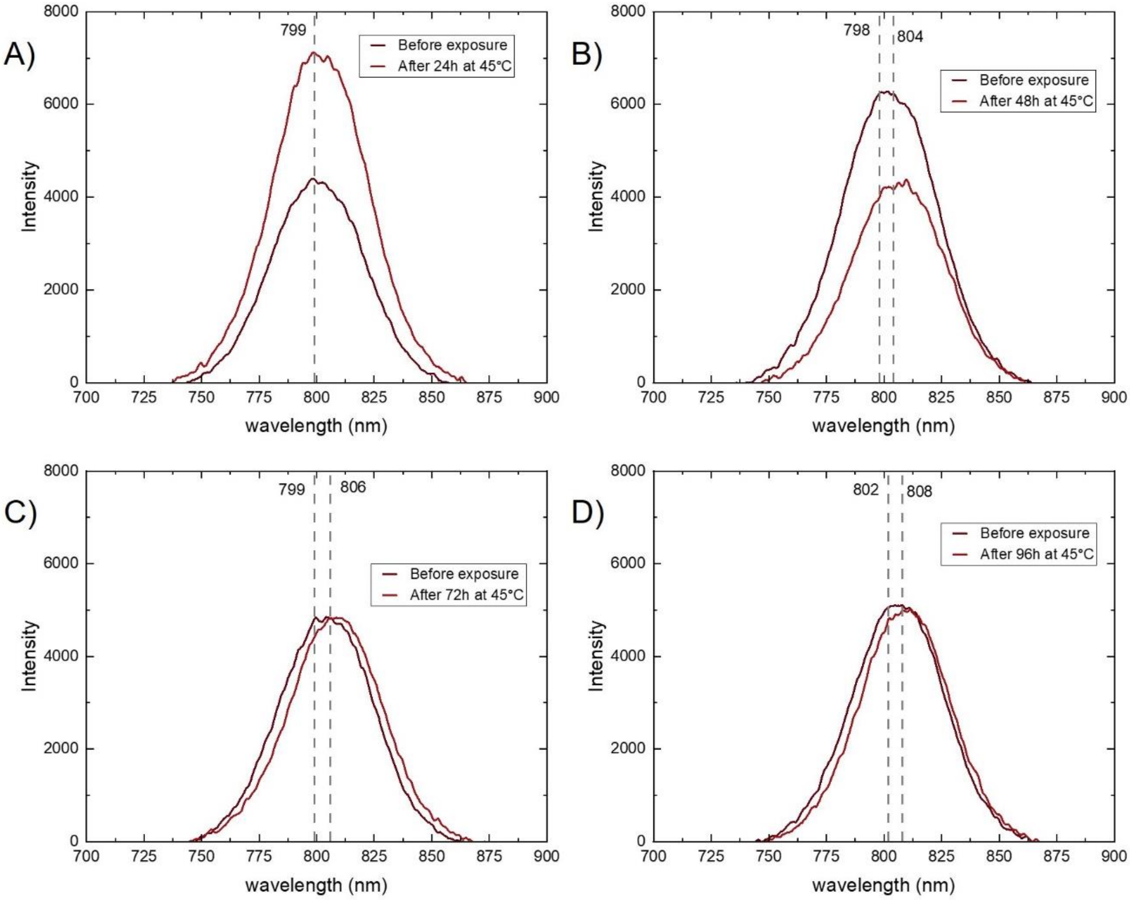
Correspondence to: Prof. Nicholas Rolston, Renewable Energy Materials and Devices Lab, School of Electrical, Computer and Energy Engineering (ECEE), Arizona State University, 7700 S River Pkwy, Tempe, AZ 85284, USA. E-mail: nicholas.rolston@asu.edu

Mobile Ion Concentration (N_o) Calculations

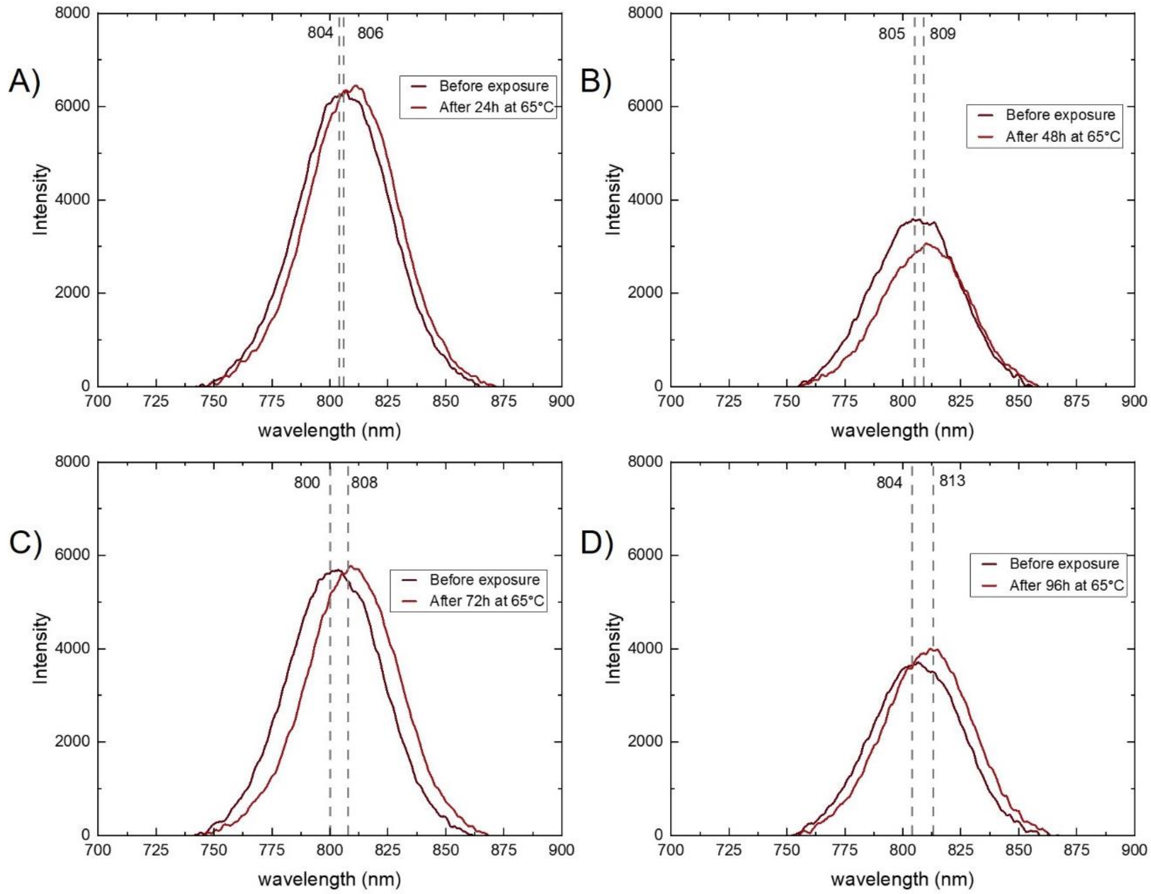
In this paper, N_o was calculated using a macro-enabled excel spreadsheet (attached an additional supplemental file) that was created to automatically determine mobile ion concentration data. The macro used the transient dark current measured with PAIOS in the form of a text file along with a designated device area and thickness as input in the main spreadsheet. It calculates N_o by first parsing the current and time measurements obtained from the text file and then performing the data analysis mentioned previously in the experimental section on said data. Once this is done, the macro outputs the values into the main sheet. The raw and processed text file data is also outputted into separate sheets for debugging purposes.



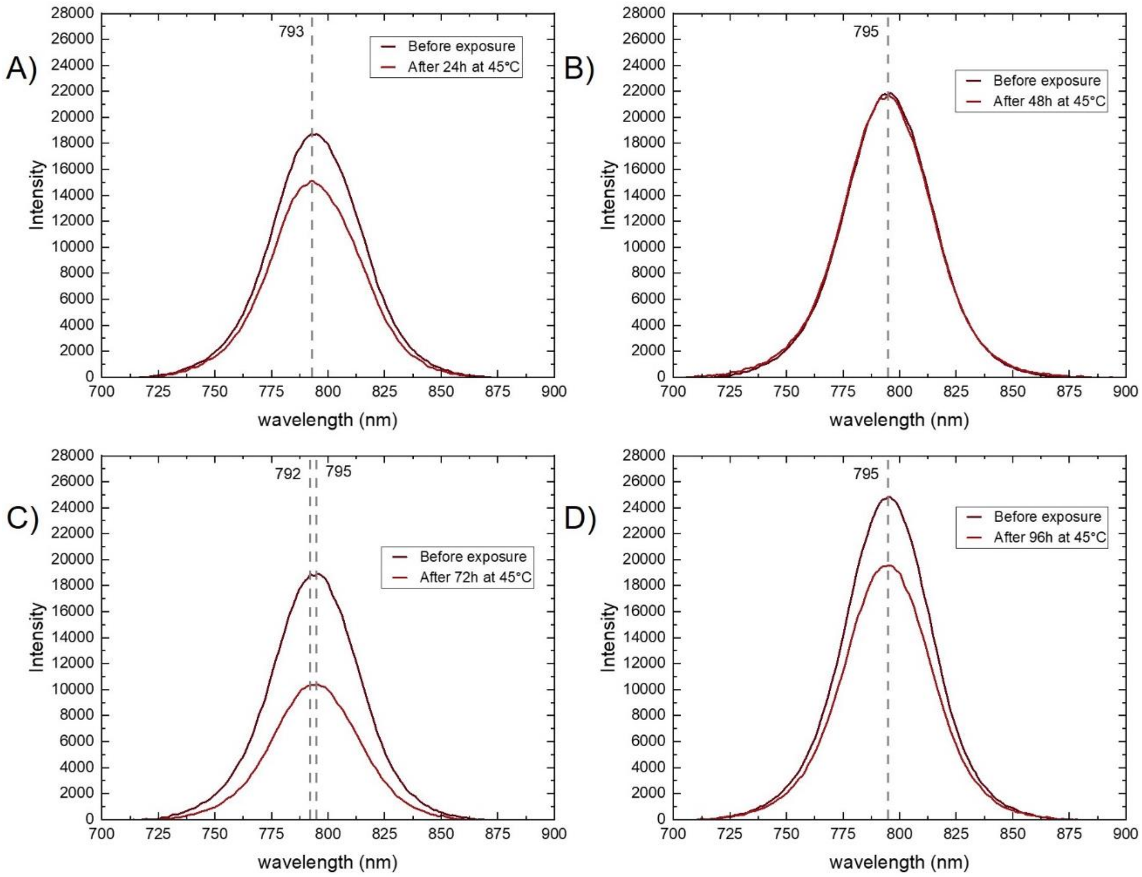
Supplementary Figure 1. Visual representation of MHP thin films at different time stamps (24h, 48h,72h,96h) captured using a camera. These films were aged at 85°C for a period of 96h on a hot plate. The pictures show evident degradation in the MHP films in the form of yellowing even after aging for just 48h. Hence it was decided that the temperature of 85°C is too damaging for the MHP thin films.



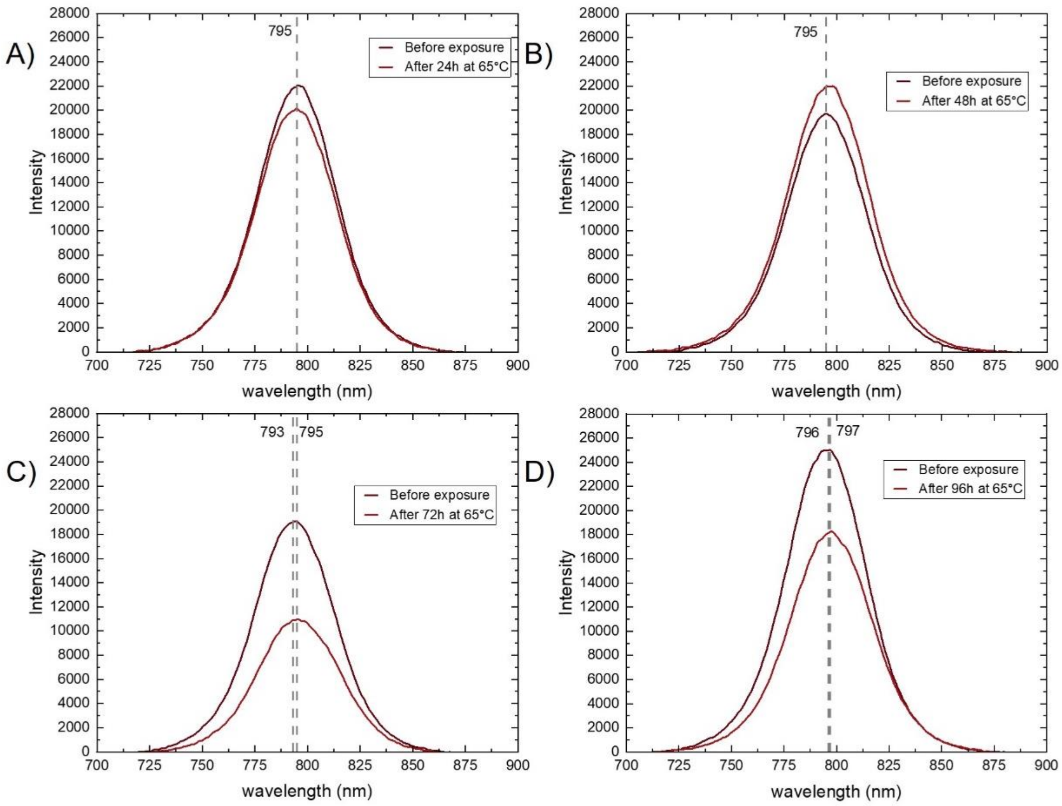
Supplementary Figure 2. Photoluminescence (PL) plots of $Cs_{0.2}FA_{0.8}PbI_3$ films aged at 45°C for a period of 96h without a glass substrate on top. There is a visible redshift after aging in the films. However, there is no consistent change in the intensity with aging. Hence it was decided that a glass substrate should be placed on top of the thin films to emulate a device-like structure. A) PL after 24h at 45°C B) PL after 48h at 45°C C) PL after 72h at 45°C D) PL after 96h at 45°C.



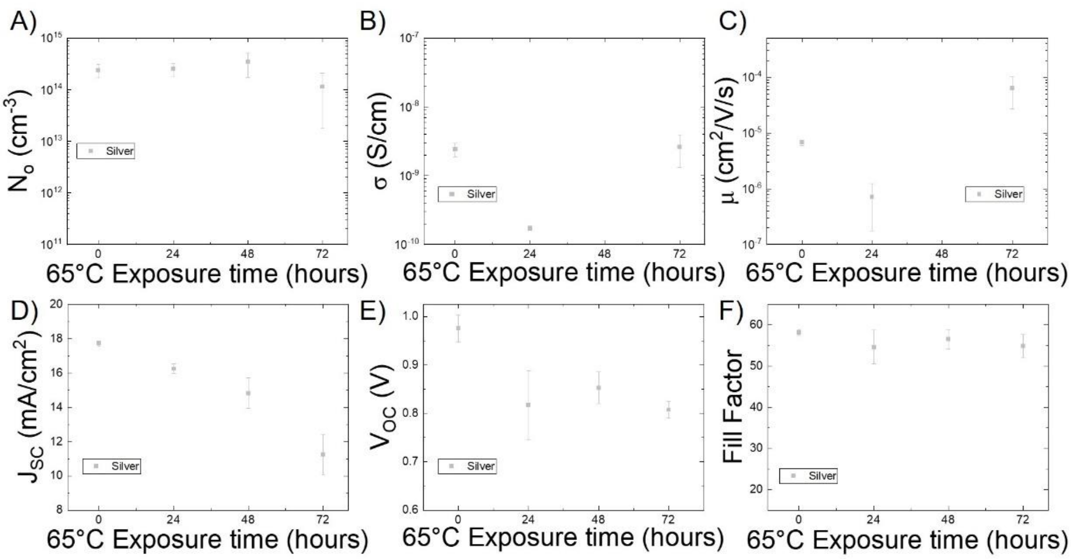
Supplementary Figure 3. PL plots of $Cs_{0.2}FA_{0.8}PbI_3$ films aged at 65°C for a period of 96h without a glass substrate on top. There is a visible redshift after aging in the films. However, there is no consistent change in the intensity with aging. Hence it was decided that a glass substrate should be placed on top of the thin films to emulate a device-like structure. A) PL after 24h at 65°C B) PL after 48h at 65°C C) PL after 72h at 65°C D) PL after 96h at 65°C.



Supplementary Figure 4. PL plots of $Cs_{0.2}FA_{0.8}PbI_3$ films aged at 45°C for a period of 96h with a glass substrate on top of them. Changes in the PL are much more consistent with a glass substrate on top of thin film while aging. A) PL after 24h at 45°C B) PL after 48h at 45°C C) PL after 72h at 45°C D) PL after 96h at 45°C.



Supplementary Figure 5. PL plots of $Cs_{0.2}FA_{0.8}PbI_3$ films aged at 65°C for a period of 96h with a glass substrate on top of them. Changes in the PL are much more consistent with a glass substrate on top of thin film while aging. A) PL after 24h at 65°C B) PL after 48h at 65°C C) PL after 72h at 65°C D) PL after 96h at 65°C.



Supplementary Figure 6. Ionic and electronic properties of PSCs with Ag electrode as shown in **Figure 4** after exposure to 65°C for 72 hours A) Mobile ion concentration (N_o) vs time B) Ionic Conductivity (σ) vs time C) Ionic Mobility (μ) vs time D) J_{SC} vs time E) V_{OC} vs time F) Fill Factor vs time

Supplementary Table 1. Shift in the PL wavelength towards the right side after aging at 45°C and 65°C respectively at each of the time stamps (24h, 48h, 72h, 96h)

Time	Shift in PL wavelength (nm) at 45°C	Shift in PL wavelength (nm) at 65°C
After 24h	0	2
After 48h	6	4
After 72h	7	8
After 96h	6	9

Supplementary Table 2. Shift in the PL wavelength (very minimal change) after aging at 45°C and 65°C respectively (with a glass substrate on top) at each of the time stamps (24h, 48h, 72h, 96h).

Time	Shift in PL wavelength (nm) at 45°C	Shift in PL wavelength (nm) at 65°C
After 24h	0	0
After 48h	0	0
After 72h	3	2
After 96h	0	1

Supplementary Table 3. Resistance tables show increasing series resistance with silver over time with an overall 10 times lower shunt resistance than the carbon electrode excluding the 48-hour measurement. Carbon maintains a relatively constant series resistance with a slight increase in shunt resistance from 0 to 72 hours.

	Carbon Electrode		Silver Electrode	
Aging Time (hours)	Series Resistance (R_s) (Ω)	Shunt Resistance (R_{sh}) (Ω)	Series Resistance (R_s) (Ω)	Shunt Resistance (R_{sh}) (Ω)
0	382	2.68×10^6	67.8	4.89×10^5
24	519	3.05×10^6	65.5	3.52×10^5
48	287	3.97×10^6	76.9	8.19×10^3
72	416	3.69×10^6	245	2.87×10^5