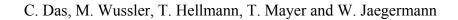
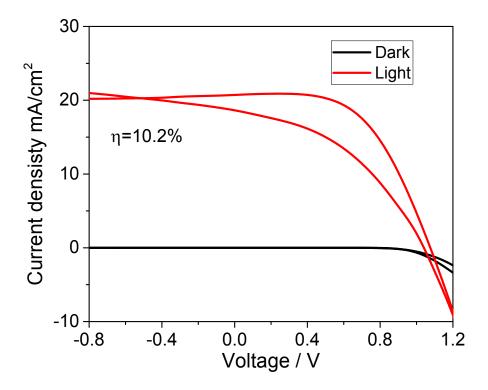
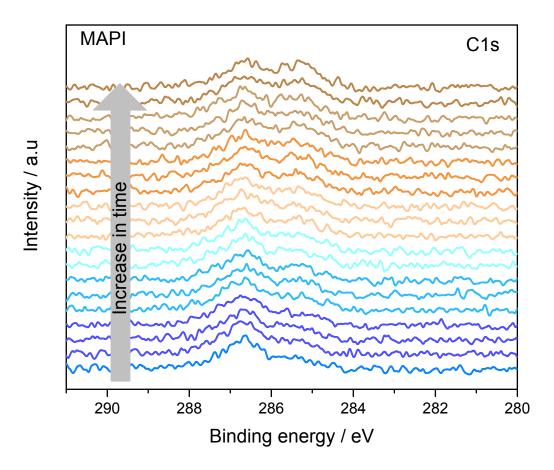
In-situ XPS study of the surface chemistry of MAPI solar cells under operating conditions in vacuum

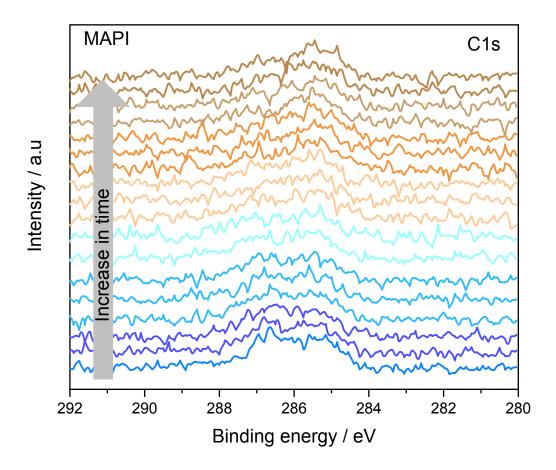




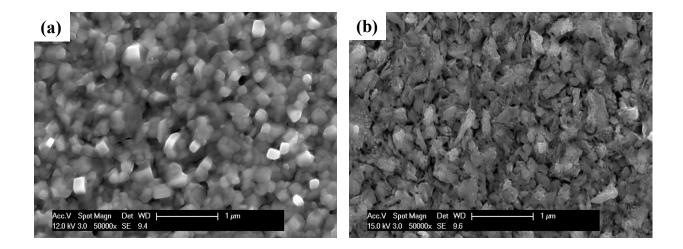
**Figure S1.** The I-V curve of the mesoporous based standard (FTO/TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/Spiro-MeOTAD/Au) perovskite solar cell.



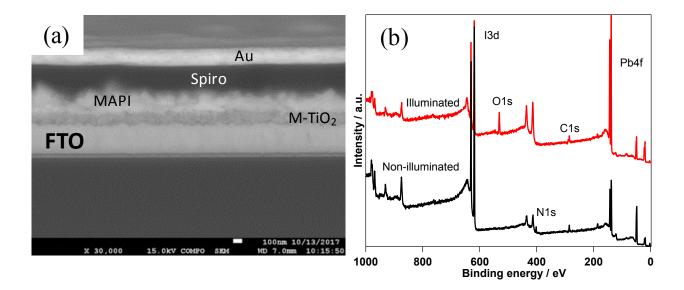
**Figure S2**. The core level photo emission spectra of C1s of MAPI in dark. Each spectrum is collected in one hour interval in order to observe the surface chemical properties of MAPI over time in dark in the vacuum. The peak at lower binding energy increases over the time indicating a slight change in surface chemical properties of MAPI surface.



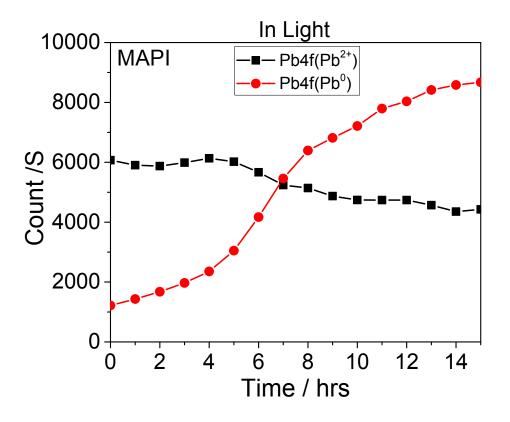
**Figure S3.** The core level photoelectron spectra of C1s of MAPI under illumination. Each spectrum is collected in one hour interval in order to observe the surface chemical properties of MAPI over time under illumination in the vacuum. The f C1s the spectrum has as two peaks having higher intensity at higher binding energy. Over the time under illumination the intensity of the C1s peaks are altered. The change in carbon spectra show that light induces the change in perovskite electronic and chemical properties.



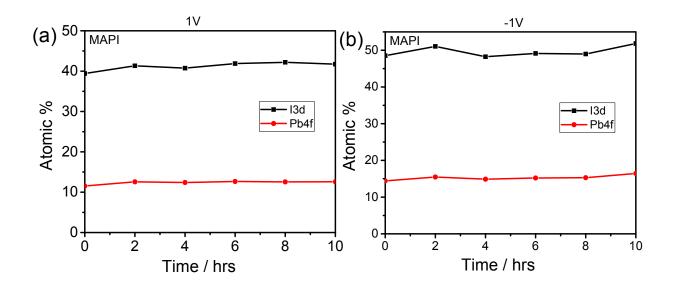
**Figure S4**: SEM images of MAPI surface without any illumination (a) and after illumination for a long time (b). It can be seen that the non-illuminated MAPI has morphology of cubic structure while the illuminated MAPI has destroyed morphology.



**Figure S5**: SEM images of a cross-section of MAPI solar cell (a) and XPS survey spectra of nonilluminated and visible light illuminated MAPI surface. From cross-sectional image it is visible that the MAPI thickness is around 200nm on the mesoporous  $TiO_2$ . In the XPS spectra of the non-illuminated and the illuminated MAPI the Ti2p core level spectra are not visible.



**Figure S6.** The absolute intensities of  $Pb^{2+}$  and  $Pb^{0}$  states in  $Pb4f_{7/2}$  photoemission line collected over 15 hours under illumination. The absolute intensities are extracted from  $Pb4f_{7/2}$  spectra in Fig. 2(b). The intensity of  $Pb^{2+}$  decreased from 6000 Count/s to 4400 Count/s while the  $Pb^{0}$  state intensity increase from 1100 Count/s to 8700 Count/s. This shows that the surface of MAPI is transferring to  $PbI_{2}$  and metallic lead with removal of organic parts in the MAPI.



**Figure S7.** The atomic concentration of lead and iodine over the time of experiment with applied potential of 1 V (a) and -1 V (b) at the gold contact on MAPI while the front contact TiO<sub>2</sub> was grounded.