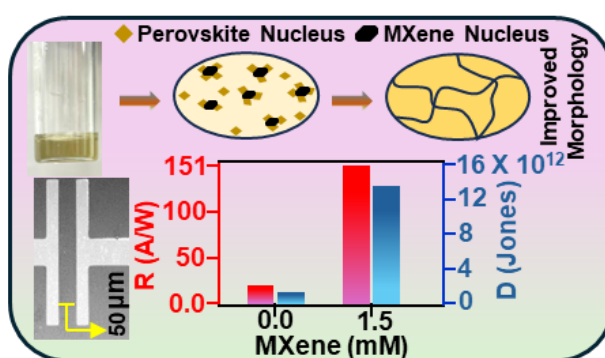


Additive Engineering of Ruddlesden-Popper Perovskites with MXene Nanoflakes: Towards Enhanced Photoresponsivity, Detectivity and Stability

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This chapter includes one-step additive engineering of Ruddlesden-Popper perovskite ($((\text{CH}_3)_2(\text{MA})_{n-1}\text{Pb}_n\text{Br}_{3n+1})$, $n=4$) absorber layer using layered $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanoflakes, which formed robust heterointerface with perovskite. The surface functional groups of MXene retard the crystallization rate of RP perovskite, thereby, spur to enhance the structural and morphological properties of RP perovskite-MXene hybrids as compared to pristine perovskite. The heterointerface between RP perovskite and MXene hybrid ($n=4 + 1.5 \text{ mM MXene}$) resulted in improved extraction of photoelectrons from RP perovskite to MXene which is confirmed by the photoluminescence (PL) quenching, time resolved PL as well as electrochemical impedance spectroscopy (EIS) results. Consequently, hybrid photodetector, without any encapsulation, revealed responsivity of $\sim 1.5 \times 10^2 \text{ A/W}$ and detectivity of $\sim 8.99 \times 10^{15} \text{ cmHz}^{1/2}/\text{W}$ at 2.0 V bias under laser illumination ($\lambda_{\text{ex}} \sim 405 \text{ nm}$, $P_{\text{in}} \sim 0.62 \text{ mW/cm}^2$) which are ~ 8.4 and ~ 7.5 times higher respectively as compared to pristine photodetector. Transient photocurrent response, measured under ambient air under similar bias and incident illumination, has shown stable peak photocurrent response after 50 cycles for hybrid photodetector, whereas peak photocurrent response of pristine photodetector has degraded by $\sim 34.74 \%$. This work offers a unique platform to explore the additive engineering of RP perovskite with wide range of MXenes to overcome the stability issues associated with perovskites and develop their high performance optoelectronic devices.

6.1 General characteristics of 2D MXene for their potential application in MHP based Optoelectronic devices

Recently, MXene of type $Ti_3C_2T_x$, which is classified as ‘unlike metallic layered solid’, [Mohammadi et al., 2021] have drawn great attention due to their excellent electrical conductivity like metals ($\sigma \sim 2.0 \times 10^4 \text{ S cm}^{-1}$), [Mathis et al., 2021] improved charge carrier mobility ($\mu_e \sim 1.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), [Dillon et al., 2016] charge carrier density ($n_e \sim 3.8 \times 10^{22} \text{ cm}^{-3}$), [Dillon et al., 2016] and tunable work function ($\phi = 1.6\text{-}5.8 \text{ eV}$). In addition, the ease of fabrication at low temperature utilizing wide range of available solvents makes them cherry on top for the formation of robust heterointerface as well as Ohmic contact or Schottky junction for potential device applications [Chen et al., 2021; Iqbal et al., 2021]. Attributed to such interesting physical properties, recently MXene is explored as an additive to improve the optoelectronic properties of MHPs because of their hydrophilic surface functional groups (T_x such as -OH, -F, -O), which are not present in other solution processed additives. This leads to a better integration of MXene with RP perovskite due to the formation of ionic bonds with lead halide as well as smaller cations present in the perovskite unit cell [Agresti et al., 2019]. For instance, in 2018, Guo et al. presented first report on the additive engineering of the bulk perovskite $CH_3NH_3PbI_3$ precursor solution using $Ti_3C_2T_x$ MXene nanoflakes and demonstrated an improvement in power conversion efficiency (PCE) of perovskite solar cell from 15.54% to 17.41% attributed to enhanced perovskite grain size [Guo et al., 2018]. Furthermore, Pan et. al. (2019) and Zhang et. al. (2020) respectively demonstrated the nano crystal growth of $CsPbBr_3$ and $CH_3NH_3PbBr_3$ on $Ti_3C_2T_x$ nanosheets through in-situ solution growth method [Pan et al., 2019; Zhang et al., 2020b]. This process has resulted in the formation of perovskite/MXene heterostructure and enabled the efficient injection of photo-electrons from perovskite to MXene, therefore enhanced the photocurrent. The use of MXene nanosheets has also been demonstrated as electron transport layer (ETL), [Yang et al., 2019a] hole transport layer (HTL), [Chen et al., 2019c] or as an additive for transport layers [Hou et al., 2021; Huang et al., 2020; Li et al., 2021b; Yang et al., 2019b, 2021; Zheng et al., 2021] for PV devices.

As discussed in **chapter 1**, the RP perovskites show interesting photo physical properties with enhanced structural stability against moisture as compared to 3D counterpart, however the presence of large organic spacer cation results in low device efficiencies which remains a bottleneck for their widespread use as an optoelectronic material. Therefore, we aim to leverage the excellent physical properties of MXene to significantly enhance the performance of 2D MHP-based optoelectronic devices through additive engineering with MXene nanoflakes.

6.2 Morphological Properties of MXene and RP Perovskite-MXene hybrids

6.2.1 Surface morphology for bulk MAX phase, Etched MAX phase, MXene nanosheets and MXene nanoflakes

The $Ti_3C_2T_x$ MXene nanosheets were synthesized from Ti_3AlC_2 MAX phase. The detailed synthesis procedure for $Ti_3C_2T_x$ MXene nanosheets is given in **Sub-Section 2.3.2 of Chapter 2**. Briefly, Ti_3AlC_2 MAX phase powder is stirred in HF solvent which allows in-situ etching of the imbedded Al layer and forms the $Ti_3C_2T_x$ etched MAX phase. Next, the MXene nanosheets were obtained from the etched MAX phase after delamination process which includes ultrasonication and centrifugation processes. FESEM image of Ti_3AlC_2 MAX phase bulk particle shows their random size with rock stone-like morphology (**Figure 6.1a**), whereas HF treated MAX phase particles, i.e., etched $Ti_3C_2T_x$ MAX phase possess multilayered loosely packed accordion-like structures with sharp edges (**Figure 6.1b**) [Sheng et al., 2021]. Next, the etched MAX phase particles were stirred in DMSO, followed by multi-step centrifugations to remove the solvent. The DMSO treated etched MAX phase particles were added in DI water and kept for ultrasonication where the water molecules were able to easily intercalate between layers of accordion-like structure and exfoliated them into nanosheets (**Figure 6.1c**). Afterwards, the MXene nanosheets suspended in DI water were ultrasonicated followed by centrifugation to obtain the MXene nanoflakes. As observed, the FESEM image of MXene nanoflakes have lateral dimensions of 50-100 nm (**Figure 6.1d**).

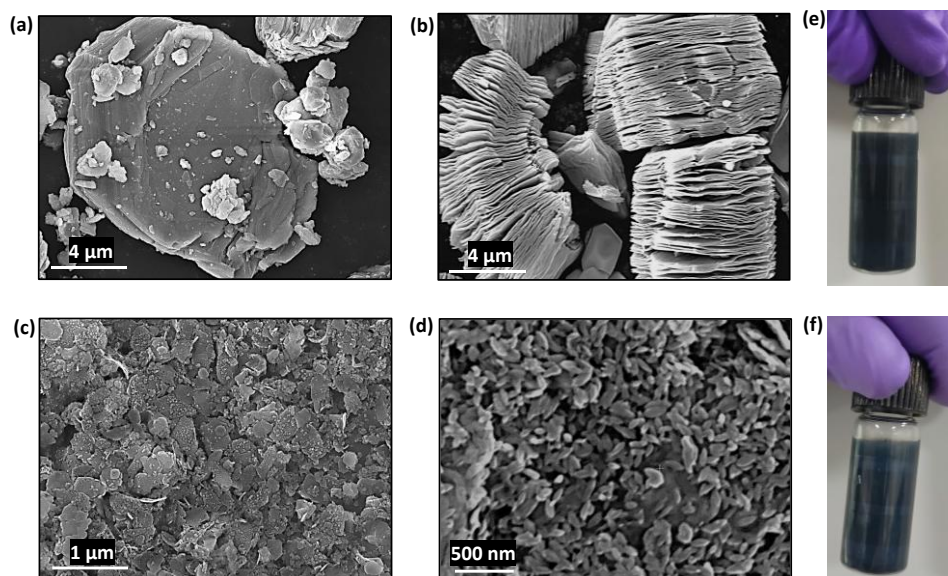


Figure 6.1 FESEM image for (a) Ti_3AlC_2 bulk MAX phase powder, (b) etched $\text{Ti}_3\text{C}_2\text{T}_x$ MAX Phase powder, (c) dropcasted $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanosheets, and (d) dropcasted $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanoflakes. Camera images for MXene nanoflakes suspension taken (e) immediately after magnetic stirring and (f) after keeping on rest for 7 days. The suspension has 4 mg/ml or 7.5 mM concentration in 4 ml DMF.

In addition, the MXene nanoflakes suspension remains stable in DMF even after seven days (**Figure 6.1e-f**), which will be beneficial to get uniform RP perovskite-MXene hybrid solution (**see Sub-Section 2.4.2 in Chapter 2 for more details**).

6.2.2 Elemental composition for bulk MAX phase and etched MAX phase powder

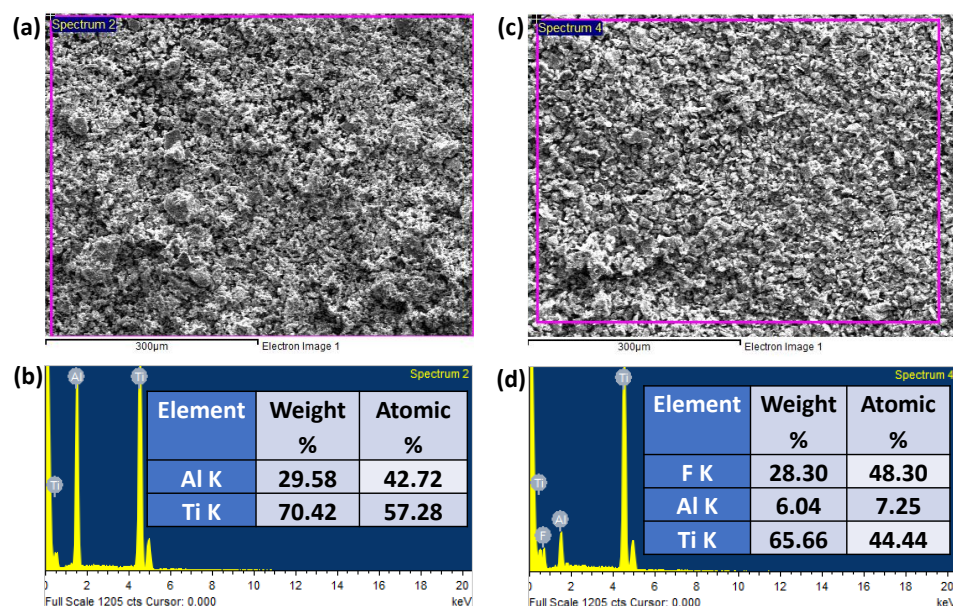


Figure 6.2 SEM images and corresponding EDAX spectrums for (a-b) Ti_3AlC_2 MAX phase powder and (c-d) etched MAX phase powders. Insets in figure (b) and (d) shows corresponding weight/atomic percentage of different elements under the scanned area shown by pink square box in figure (b) and (d) respectively.

The EDAX spectra of MAX phase and etched MAX phase are investigated to confirm the reduction of Al layer. This measurement confirms the reduction of Al (atomic % reduced from 42.72 to 7.25) due to the etching of embedded Al layer, as well as the introduction of F (atomic % = 48.30) as a surface functional group (**Figure 6.2a-d**).

6.2.3 TEM analysis for MXene nanoflakes

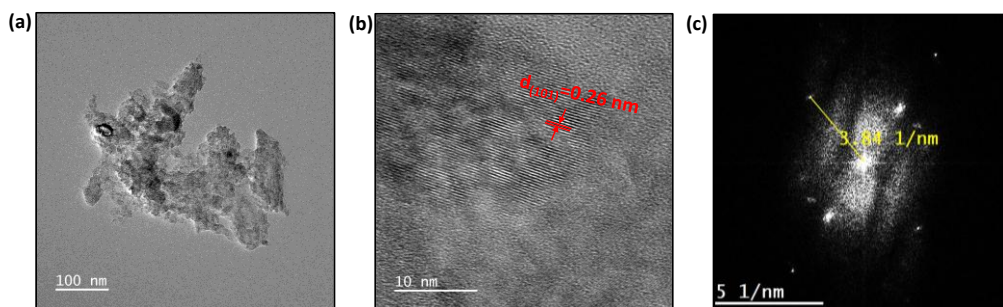


Figure 6.3 (a) Low magnification TEM image, (g) HR-TEM image and (h) Selected area electron diffraction pattern for MXene nanoflakes.

The sample preparation method is discussed in **Sub-Section 2.9.2** of **Chapter 2**. Low magnification TEM image of MXene nanoflakes has shown thin crumpled layer structures (**Figure 6.3a**). Moreover, the HR-TEM image has shown the presence of atomic planes with d-spacing ~ 0.26 nm (**Figure 6.3b**). Such d-spacing corresponds to a XRD peak at $2\theta=35.14^\circ$ with (101) plane as discussed below in the **structural section 6.3.1**. In addition, the selected area electron diffraction pattern confirms the crystalline nature of nanoflakes and above-mentioned atomic d-spacing (**Figure 6.3c**).

6.2.4 Effect of MXene concentration on the Surface Morphology of RP perovskite-MXene hybrid Thin film

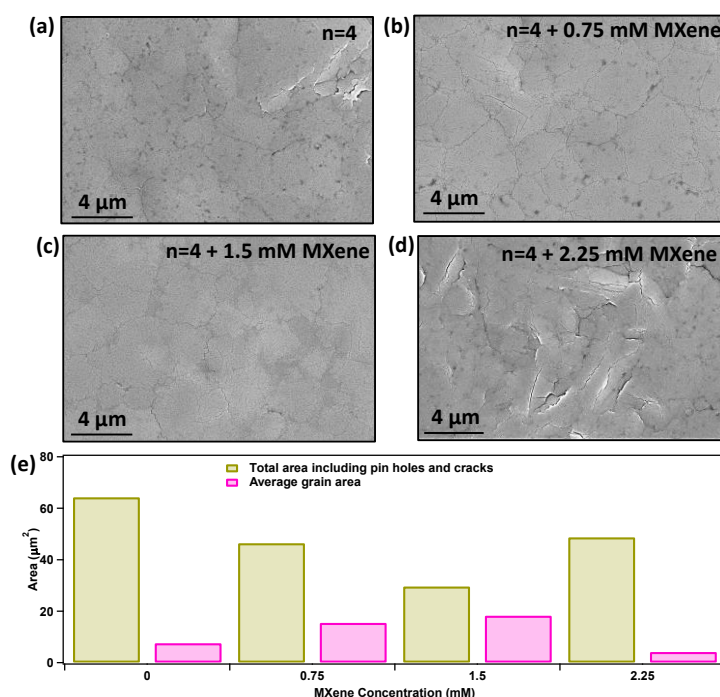


Figure 6.4 FESEM images for (a) pristine RP perovskite ($n=4$) and (b-d) hybrid ($n=4$ + MXene: 0.75 mM, 1.5 mM) perovskites. (e) Variation in the area of pin holes + cracks as well as average grain size over the film with MXene concentration. These parameters are estimated from FESEM images using Image-J software.

The thin film preparation method is discussed in **Sub-Section 2.5.2** of **Chapter 2**. The top view FESEM images for pristine RP perovskite ($n=4$) thin film and hybrids ($n=4$ + MXene: 0.75 mM, 1.5 mM, 2.25 mM) are recorded to investigate the difference in surface morphology. The pristine ($n=4$) thin film has shown a sheet-like structure with smaller grain size and large number of pin holes (**Figure 6.4a**). As estimated using the Image-J software, the average area of grain is $\sim 7.5 \mu\text{m}^2$ (**Figure 6.4e**). In

contrast, hybrid thin films have revealed significantly enhanced average grain area of $\sim 15.47 \mu\text{m}^2$ and $\sim 18.25 \mu\text{m}^2$ with the addition of 0.75 mM and 1.5 mM additives respectively (**Figure 6.4b-c & Figure 6.4e**). Moreover, the total area corresponding to pin holes and cracks over the film has reduced from $\sim 64.27 \mu\text{m}^2$ to $\sim 29.57 \mu\text{m}^2$ with the addition of 1.5 mM additives in pristine perovskite thin film.

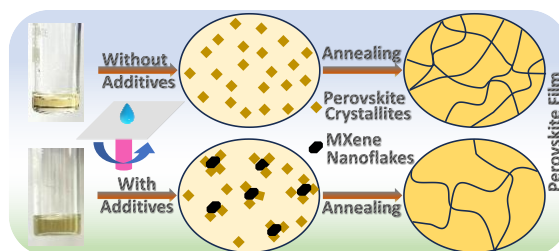


Figure 6.5 Schematic representation showing the nucleation process during annealing of pristine and hybrid perovskite during spin coating.

This is due to suppression of perovskite crystallites growth across entire film and initiation around MXene nanoflakes as shown in the nucleation process schematic (**Figure 6.5**) leading to the formation of robust heterointerface. As a result, there is a retardation in crystallization rate of MXene added RP perovskite thin films which promote the uniform crystal growth and improved overall morphology, as reported elsewhere for bulk MHPs [Guo et al., 2018]. Such improved morphology facilitate least resistive path for transportation of photo charge carriers via heterointerface [Guo et al., 2022]. Finally, excessive presence of MXene additives (2.25 mM) has extruded the film surface, resulting in large number of pin holes and cracks ($\sim 48.69 \mu\text{m}^2$) over the film (**Figure 6.4d & Figure 6.4e**). These studies have demonstrated that hybrid ($n=4 + 1.5 \text{ mM}$ MXene) thin film exhibits better structural and morphological characteristics than the pristine $n=4$ thin film. Therefore, further investigations are performed primarily for pristine and hybrid ($n=4 + \text{MXene: } 0.75 \text{ mM \& } 1.5 \text{ mM}$) thin films only.

6.2.5 Elemental composition for pristine RP perovskite and RP perovskite-MXene hybrid thin films

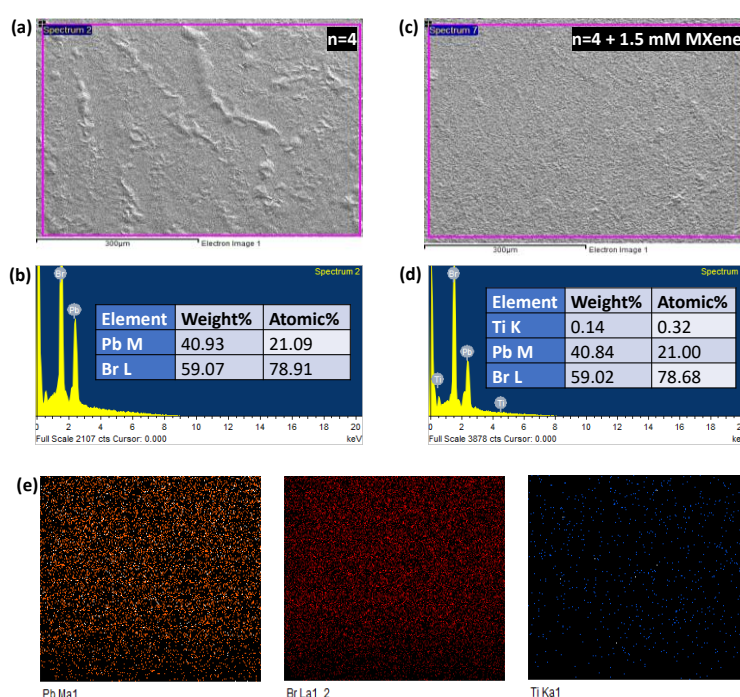


Figure 6.6 SEM image and corresponding EDAX spectrum for (a-b) pristine ($n=4$) and (c-d) hybrid ($n=4 + 1.5 \text{ mM}$ MXene) hybrid thin films. Insets of figure (b) and (d) shows corresponding weight/atomic percentage of

different elements under the scanned area shown by pink square box in figure (a) and (c) respectively. (e) Elemental mapping for Pb, Br and Ti.

The EDAX measurements are carried out for pristine RP perovskite ($n=4$) thin film and hybrid ($n=4 + 1.5$ mM MXene) to investigate the elemental composition and their spatial distribution (**Figure 6.6a-e**). EDAX spectrum and relative elemental composition analysis for pristine thin film has shown the signature of lead (Pb; atomic % = 21.09) and bromine (Br; atomic % = 78.91) elements. Whereas hybrid ($n=4 + 1.5$ mM MXene) film has shown the presence of titanium (Ti; atomic % = 0.32) along with lead (Pb; atomic % = 21.00) and bromine (Br; atomic % = 78.68) elements. The low atomic percentage of Ti as compared to other elements of perovskite confirm the controlled additives engineering of MXene nanoflakes in $(\text{CH})_2(\text{MA})_3\text{Pb}_4\text{Br}_{13}$ thin films.

6.3 Structural properties

6.3.1 Crystal structure for bulk MAX phase and etched MAX phase powders

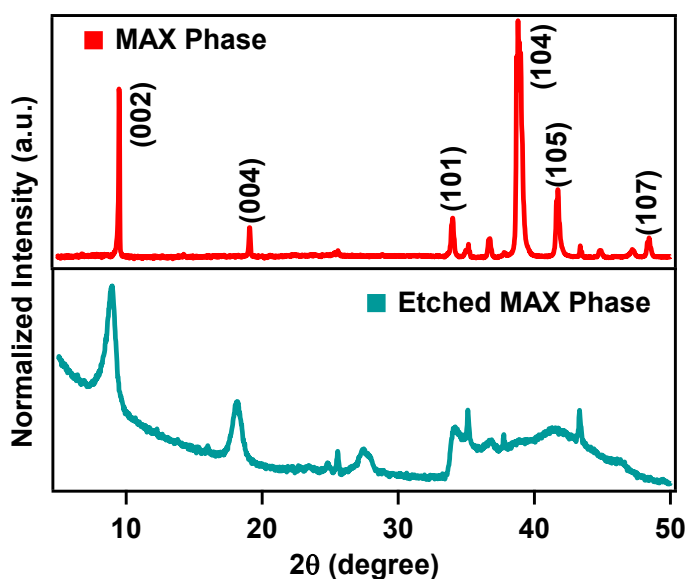


Figure 6.7 XRD diffraction patterns for MAX phase and etched MAX phase powders.

Crystallographically, each C atom is surrounded by six Ti atoms, forming an octahedron. Similarly, six Al atoms coordinate each Ti atom to form a hexagonal prism. i.e., it can be considered as an alternate stacking of $n\text{TiC}$ layers made up of edge-shared CTi_6 octahedrons and one TiAl layer made up of edge-shared Ti_6Al triangular prisms [Chen et al., 2019b]. Moreover, one and two TiC layers can be merged to form edge-shared monolayer and bilayers in the 211 and 312 phases, respectively. The XRD patterns of Ti_3AlC_2 MAX phase bulk particles and the etched MAX phase again confirm the topochemical synthesis of $\text{Ti}_3\text{C}_2\text{T}_x$ etched MAX phase (**Figure 6.7**) because most intense peak at $2\theta=38.82^\circ$, corresponding to the (104) crystal plane in Ti_3AlC_2 MAX phase disappeared after HF treatment. Moreover, the first characteristic peak at $2\theta=9.54^\circ$, corresponding to the (002) crystal plane in the MAX phase, has shifted towards a lower diffraction angle at $2\theta = 8.93^\circ$ in the etched MAX phase after HF treatment [Ansari et al., 2025].

6.3.2 Crystal structure for pristine RP perovskite and perovskite-MXene hybrid thin films

The schematic for the crystal structure schematic of RP perovskite $(\text{CH})_2(\text{MA})_3\text{Pb}_4\text{Br}_{13}$ is shown in **Figure 6.8a**, where, four-corner sharing $[\text{PbBr}_6]$ octahedra layers form a three-dimensional network and are separated by hydrophobic cyclic organic spacer cations CH. This separation results in stabilizing the crystal structure, enhanced moisture resistance with unique optoelectronic properties. Moreover, the MA cations are caged between $[\text{PbBr}_6]$ octahedrons. The RP perovskite material is

synthesized using two step sol-gel method in acidic medium as mentioned earlier (see Sub-Section 2.1.3 of Chapter 2 for more details) [Rahil et al., 2023]. Thin film XRD patterns are recorded to examine the crystal structure and crystallinity for pristine RP perovskite ($n=4$) and hybrids ($n=4 + \text{MXene}$: 0.75 mM, 1.5 mM, 2.25 mM). The XRD pattern for pristine $n=4$ thin film has shown three diffraction peaks at $2\theta = 11.99^\circ$, 15.20° and 30.36° which correspond to (060), (110) and (220) crystal planes respectively (Figure 6.8b, red curve) [Rahil et al., 2023]. Whereas the XRD pattern of hybrids ($n=4 + \text{MXene}$: 0.75 mM, 1.5 mM, 2.25 mM) demonstrated that the (060) peak is shifted by $2\theta=0.73^\circ$ (from 11.99° to 12.26°) towards the lower angle, while the positions of the other two XRD peaks remain unchanged (Figure 6.8b, yellow curve, blue curve, green curve). Such shift in the XRD peak is attributed to the stress caused by MXene additives, suggesting that perovskite crystal experienced strain during crystallization process.

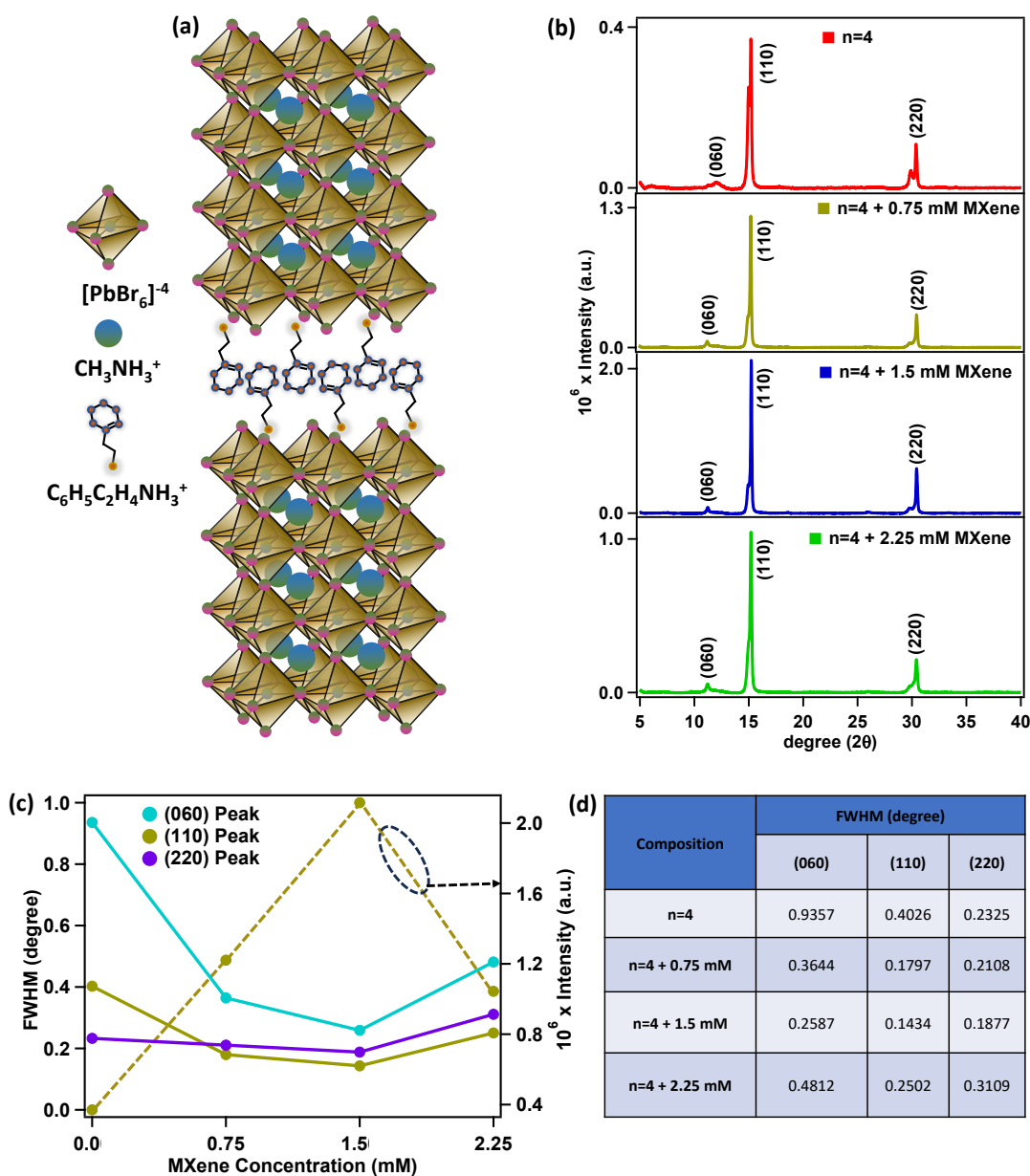


Figure 6.8 (a) Schematic diagram showing the crystal structure of RP perovskite $(\text{CH}_3)_2(\text{MA})_3\text{Pb}_4\text{Br}_{13}$, ($n=4$). (b) XRD patterns for pristine ($n=4$) and hybrid ($n=4 + \text{MXene}$: 0.75 mM, 1.5 mM, 2.25 mM) perovskites. (c) Variation in FWHM (left axis) for all XRD peaks and variation in intensity for (110) XRD peak (right axis) with the MXene concentration. (d) FWHM for all peaks obtained after Gaussian fitting for pristine ($n=4$) and hybrid ($n=4 + \text{MXene}$: 0.75 mM, 1.5 mM, 2.25 mM) thin films.

This stress management prevents the formation of cracks and defects, leading to an improved structural/morphological properties of hybrid thin films as compared to pristine

counterpart. Guo Z. and coworkers have highlighted similar shift towards lower diffraction angle in the peak of MAPbI_3 at $2\theta = 14.10^\circ$ with additive engineering by MXene [Guo et al., 2018]. As the concentration of MXene additive increases from 0.75 mM to 1.5 mM, the intensity for all XRD peaks has enhanced and FWHM (calculated using Gaussian Fitting) is found to be reduced, demonstrating overall enhancement in the grain size and crystallinity of the hybrid films (**Figure 6.8c-d**). Furthermore, excessive addition of MXene (2.25 mM) results reduced intensity and larger FWHM for all XRD peaks.

6.4 Electronic properties

6.4.1 XPS spectra for pristine RP perovskite and perovskite-MXene hybrid thin film

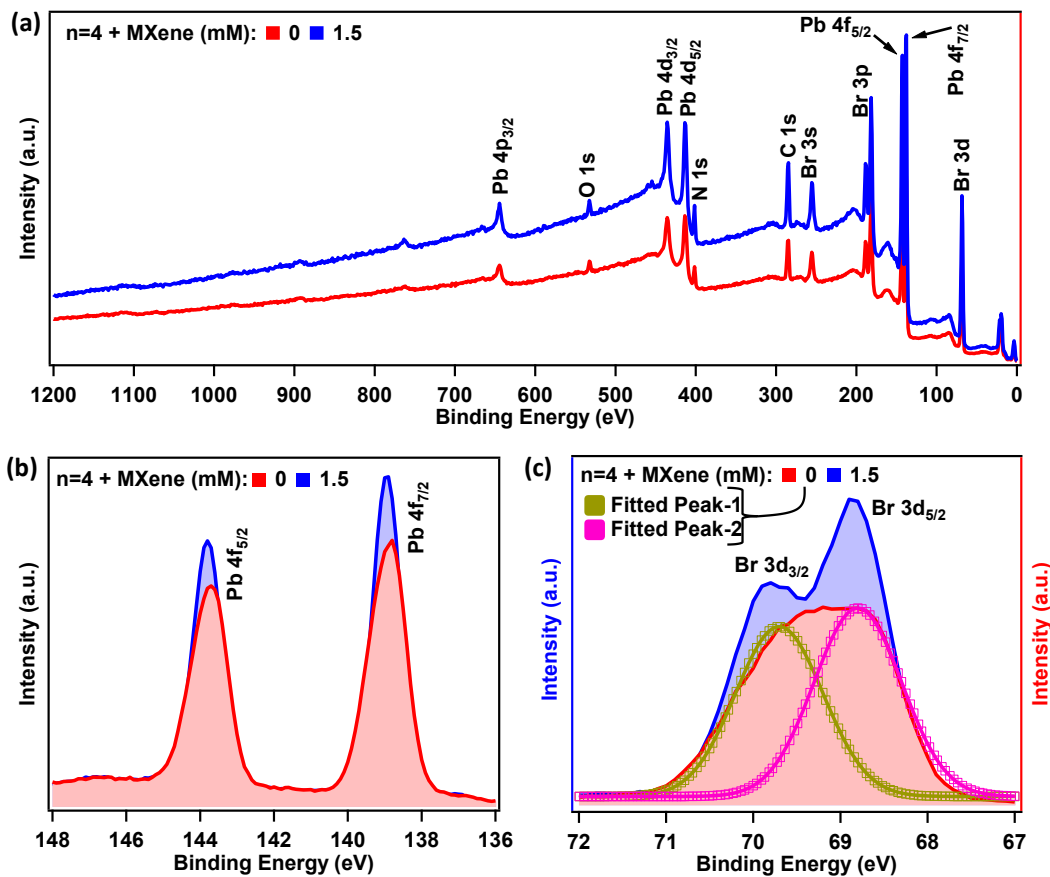


Figure 6.9 (a) XPS survey spectra, (b) High-resolution XPS spectra of Pb 4f, and (c) High-resolution XPS spectra of Br 3d orbital peak for pristine and hybrid (n=4 + 1.5 mM) perovskites.

To better understand the heterointerface between RP perovskite and MXene nanoflakes, XPS is carried out for pristine and hybrid (n=4 + 1.5 mM MXene) thin film samples. The survey spectra for pristine and hybrid (n=4 + 1.5 mM MXene) thin film has shown in **Figure 6.9a**. Moreover, high resolution XPS spectra of pristine (n=4) perovskite has shown doublet peak of Pb 4f at 138.80 eV and 143.70 eV which correspond to spin orbit splitting of Pb 4f_{7/2} and Pb 4f_{5/2} components respectively (**Figure 6.9b**) [Xie et al., 2016]. Furthermore, the doublet peak of Br 3d at 68.70 eV and 69.70 eV correspond to spin orbit splitting of Br 3d_{5/2} and Br 3d_{3/2} components respectively (**Figure 6.9c, Gaussian Fitting**) [Li et al., 2023c]. For hybrid thin film, both the doublet peaks of Pb 4f and Br 3d orbitals were found to be shifted towards higher binding energies due to the interfacial interaction between surface functional groups (T_x) (**as discussed in Section 6.1**) of MXene nanoflakes with Pb and Br of RP perovskite material. As reported elsewhere, these interfacial interactions are driven by the ionic bond formation between MXene functional groups ($-T_x$) and MHP crystallites which has

resulted in modified chemical environment of $[\text{PbBr}_6]$ inorganic octahedra [Guo et al., 2022; Liu et al., 2017].

6.4.2 UPS spectra for pristine RP perovskite and perovskite-MXene hybrid thin film

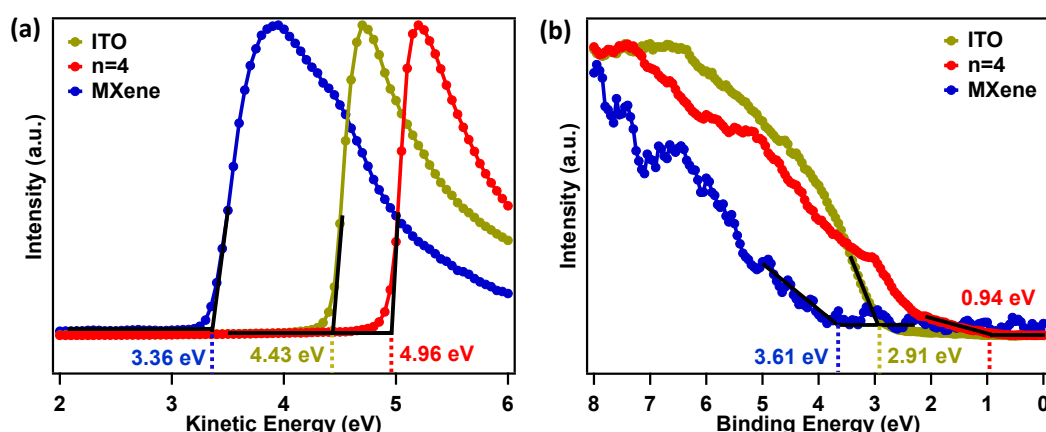


Figure 6.10 UPS for pristine ($n=4$) perovskite and MXene nanoflakes drop-casted on Indium tin oxide (ITO) showing (b) secondary electron cut-off, and (c) valence band region.

Moreover, the electronic band level of RP perovskite ($n=4$) and MXene nanoflakes were examined using UPS. The work function (ϕ) is obtained from the difference between the cutoff of the highest binding energy and the incident photon energy (21.2 eV) [Whitten, 2023]. The estimated work functions with respect to fermi level (E_f) are found to be ~ 4.96 eV and ~ 3.36 eV for pristine RP perovskite ($n=4$) and MXene nanoflakes respectively (**Figure 6.10a**). Furthermore, the VBM with respect to E_f is estimated from the cutoff of the lowest binding energy, which are found to be ~ 0.94 eV and ~ 3.61 eV for pristine RP perovskite ($n=4$) and MXene nanoflakes respectively (**Figure 6.10b**). The estimation of CBM for RP perovskite is discussed in the coming **section 6.7.1**.

6.5 Optical properties

6.5.1 UV-vis spectra for pristine RP perovskite and perovskite-MXene hybrid thin film

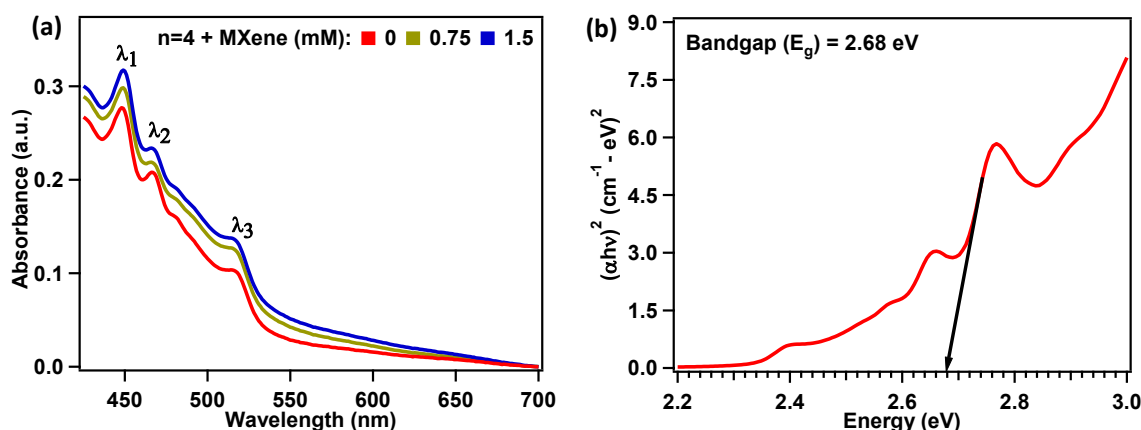


Figure 6.11 (a) UV-Visible spectra for pristine and hybrid ($n=4$ + MXene: 0.75 mM, 1.5 mM) perovskites. (b) Tauc's plot for pristine RP perovskite.

Furthermore, UV-Visible, PL and TRPL spectroscopies are investigated for pristine and hybrid ($n=4$ + MXene: 0.75 mM, 1.5 mM) thin films to understand the effect of RP perovskite-MXene heterointerface on optical properties. The UV-Visible spectrum of pristine RP perovskite thin film has

shown characteristic room-temperature exciton absorption peak at $\lambda_2=466$ nm. In addition, two exciton peaks at $\lambda_1=449$ nm and $\lambda_3=516$ nm (**Figure 6.11a**) indicate the optical absorption bands for $n=3$ and $n=\infty$ (MAPbBr₃) phases respectively. Such additional existing phase in RP perovskite has introduced broad spectral absorption features which can further enhance the optical absorption abilities under visible light illumination and thus can generate more free-charge carriers for photoconduction [Zheng et al., 2018]. The characteristic optical absorption peak corresponds to the optical bandgap of 2.68 eV as estimated from the Tauc's plot (**Figure 6.11b**). As the concentration of MXene is increased from 0.75 mM to 1.5 mM, the UV-Vis spectra of hybrid thin films have shown an enhancement in absorbance without any shift in peak positions compared to pristine RP perovskite (**Figure 6.11a**). Such increased absorption is attributed to the enhanced surface morphology and crystallinity due to the incorporation of MXene in RP perovskite which results in improved stacking of multiple quantum wells (MQWs) structures [Katan et al., 2019].

6.5.2 PL and TRPL spectra for pristine RP perovskite and perovskite-MXene hybrid thin film

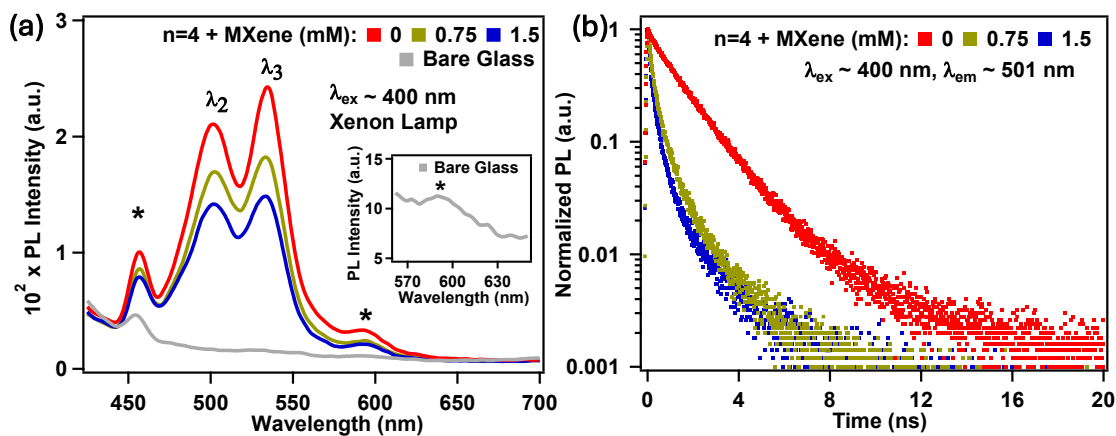


Figure 6.12 (a) PL spectra and (b) TRPL spectra for pristine and hybrid ($n=4$ + MXene: 0.75 mM, 1.5 mM) perovskites.

Like absorbance, PL spectra of pristine RP perovskite thin film has shown two distinct peaks at $\lambda_2=501$ nm and $\lambda_3=535$ nm under the excitation ($\lambda_{ex} = 400$ nm) of Xenon lamp. The remaining two peaks at 457 nm (*) and 592 nm (*) are harmonic peaks appeared due to instrument limitation which are confirmed by recording the PL spectra of bare glass substrate (**Figure 6.12a**). Furthermore, when the concentration of MXene nanoflakes is increased from 0.75 mM to 1.5 mM, the hybrid thin films demonstrated a significant PL quenching i.e., intensity of all the peaks reduced uniformly, in comparison to pristine thin film. To further understand the charge extraction kinetics, the TRPL decay profiles are obtained using TCSPC method for the characteristic emission peak wavelength ($\lambda_{em} = 501$ nm) of pristine and hybrid ($n=4$ + MXene: 0.75 mM, 1.5 mM) thin films excited by laser ($\lambda_{ex} = 400$ nm) (**Figure 6.12b**). The photo generated charge carrier recombination lifetime for pristine perovskite is estimated to be 1528 ps using double exponential fitting. Whereas, the charge carrier lifetime for hybrid is reduced to 576 ps and 442 ps when the concentration of MXene is increased from 0.75 mM to 1.5 mM respectively. The observed PL quenching and reduced charge carrier lifetimes for the hybrid thin films are attributed to the formation of more decay channel, which will provide faster dissociation of photogenerated electron-hole pairs and effective injection of photoelectrons from RP perovskite to MXene nanoflakes as confirmed by UPS measurements [Zhang et al., 2020b][Zhao et al., 2016a].

6.6 Electrochemical impedance spectroscopy for pristine RP perovskite and perovskite-MXene hybrid thin film

Furthermore, the electrochemical impedance spectroscopy (EIS) is performed under dark and illumination conditions, which reveals the reduced charge transfer resistance (R_{ct}) for hybrid ($n=4$ +

1.5 mM MXene) sample as compared to pristine sample, implying that conductivity of the perovskite film has increased with the addition of MXene nanoflakes (**Figure 6.13a-b**) [Yang et al., 2019a, 2019b].

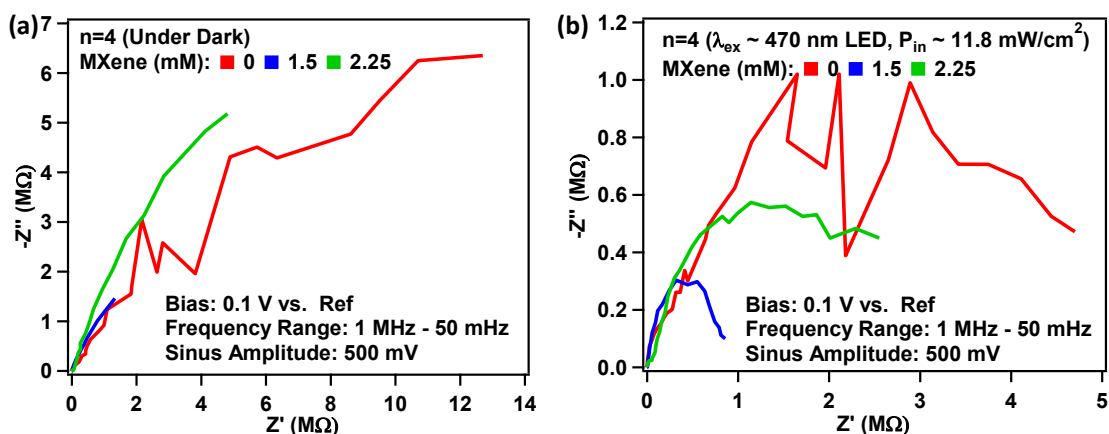


Figure 6.13 EIS spectroscopy for pristine ($n=4$) and hybrid ($n=4$ + MXene: 1.5 mM, 2.25 mM) photodetector under (a) dark and (b) LED illumination. To perform this measurement, pristine and hybrid solutions are dropcasted on FTO and bare FTO substrate is placed on the film keeping effective device area as 1×1 cm².

6.7 Optoelectronic properties

6.7.1 Photodetector fabrication and energy band diagram

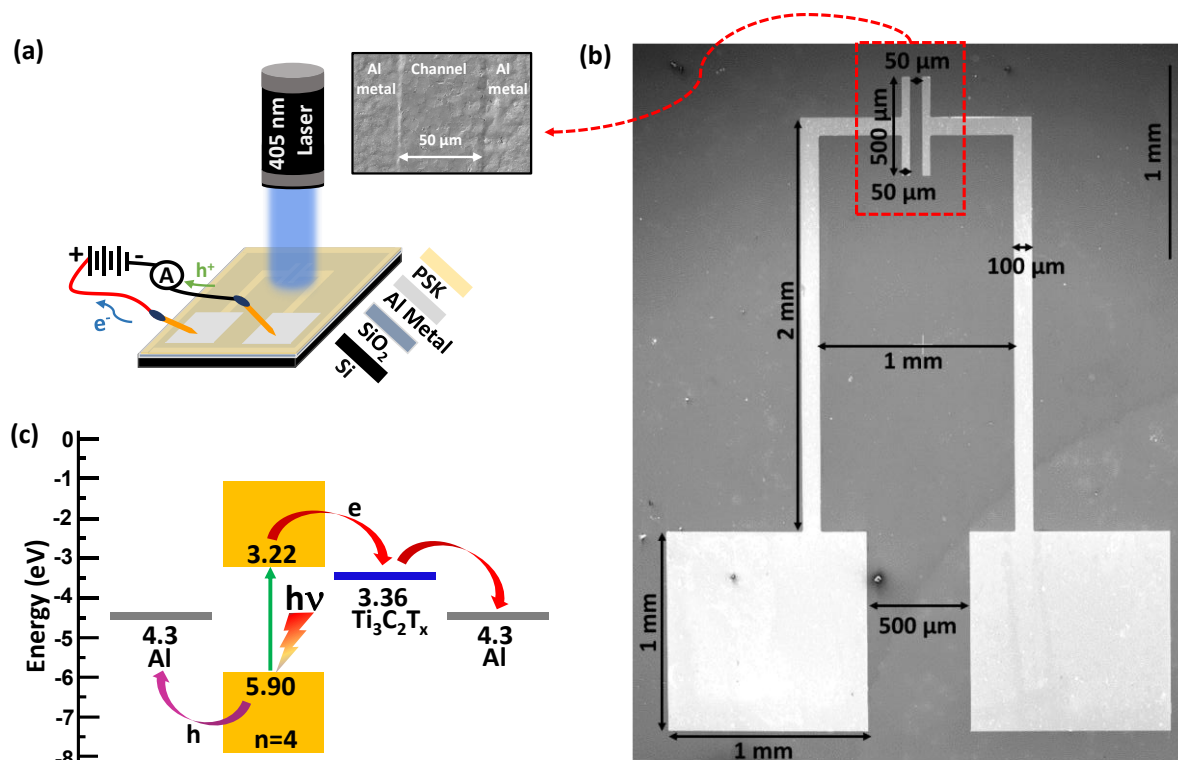


Figure 6.14 (a) Schematic representation showing photodetection measurement setup with lateral photodetector. Inset shows the FESEM image of the photodetector electrode (b) FESEM image for photodetector electrode. (c) Schematic representation showing the electronic band diagram and charge transport mechanism under illumination for hybrid ($n=4$ + MXene) perovskite. The position of VBM and CBM for perovskite and the work function for MXene nano flakes are determined using UPS.

In order to investigate the optoelectronic performance of pristine and hybrid materials I have fabricated the lateral photodetectors forming M-S-M (metal-semiconductor-metal) configuration, as shown in the schematic (**Figure 6.14a**). These photodetectors are fabricated using two-step photolithography technique on SiO₂ (100 nm) coated Si-substrate followed by etching route (see **Sub-Section 2.7.1.3 in Chapter 2 for more details**). The close view FESEM image displays the uniform coverage of spin coated RP perovskite material between the Al-metal electrodes (**Figure 6.14a, inset**) and the FESEM image shows the patterned bare electrode of photodetector with channel width of 50 μm (**Figure 6.14b**). Furthermore, energy band diagram is used to demonstrate the charge transport dynamics in these lateral photodetectors (**Figure 6.14c**). It must be noted that the VBM and CBM for RP perovskite is estimated after equating the E_f to zero and using the bandgap ($E_g \sim 2.68$ eV). The VBM and CBM for RP perovskite are found to be ~ 5.90 eV and ~ 3.22 eV, respectively. The obtained work function of MXene ($\phi \sim 3.36$ eV) falls at lower energy level than the CBM of RP perovskite, which confirms that MXene can efficiently extract the photoelectrons from RP perovskite and can work as a suitable ETM in the formed heterointerface between RP perovskite and MXene nanoflakes.

When an electric field is applied, the photogenerated electrons from RP perovskite get transported to the MXene nanoflakes due to the favorable energy landscape, and finally reach the Al current collector. On the other hand, the photogenerated holes get transported to the counter Al metal electrode to maintain the charge neutrality (**Figure 6.14c**).

6.7.2 I-V characteristics and transient photocurrent measurements for pristine RP perovskite and perovskite-MXene hybrid thin film-based photodetector under fixed incident illumination power

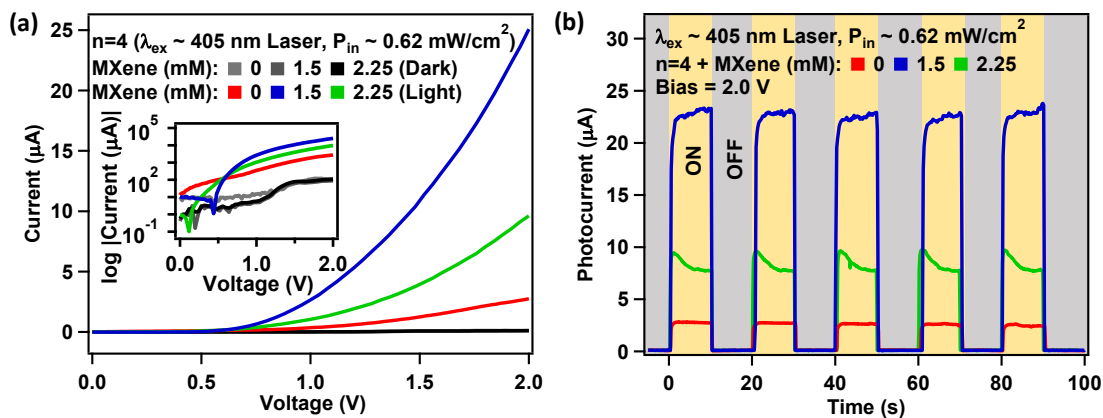


Figure 6.15 (a) Linear I-V characteristics under dark and illumination condition. The inset shows I-V characteristics in log scale. (b) Transient photocurrent response for pristine and hybrid ($n=4$ + MXene: 1.5 mM, 2.25 mM) photodetectors under the applied bias of 2.0 V. Laser light: $\lambda_{\text{ex}} \sim 405$ nm, $P_{\text{in}} \sim 0.62$ mW/cm² is used for illuminations.

The I-V characteristic of pristine and hybrid photodetectors is recorded for voltage window of 0.0 - 2.0 V under dark and illumination conditions which confirmed the semiconducting nature of the pristine and hybrid materials. The pristine and hybrid photodetectors revealed the dark currents of ~ 0.12 μA ($n=4$), ~ 0.088 μA ($n=4$ + 1.5 mM MXene) and ~ 0.11 μA ($n=4$ + 2.25 mM MXene) at an applied bias of 2.0 V (**Figure 6.15a, light grey curve, dark grey curve, and black curve**) which further enhanced to ~ 2.8 μA , ~ 25.08 μA , and ~ 9.6 μA respectively (**Figure 6.15a, red curve, blue curve, and green curve**) under CW laser illumination ($\lambda_{\text{ex}} \sim 405$ nm, $P_{\text{in}} \sim 0.62$ mW/cm²) at 2.0 V. Next, transient photocurrent measurements are performed for pristine and hybrid photodetectors under an applied bias of 2.0 V using same laser source. A manual shutter is used to switch ON and OFF the illumination at an interval of every 10 second. As anticipated from I-V characteristics, the hybrid ($n=4$ + 1.5 mM MXene) photodetector has shown significantly enhanced photocurrent of ~ 23.38 μA which is ~ 8.5 times higher as compared to the pristine photodetector photocurrent response ~ 2.76 μA (**Figure**

6.15b, red and blue curve). Further addition of MXene in the RP perovskite, i.e., hybrid (n=4 + 2.25 mM MXene), has resulted in lowering the transient photocurrent response to $\sim 9.33 \mu\text{A}$ (Figure 6.15b, green curve).

6.7.2.1 Responsivity (R), external quantum efficiency (EQE), detectivity (D) and noise equivalent power (NEP) and ON-OFF ratio for pristine and hybrid photodetector under fixed incident illumination power

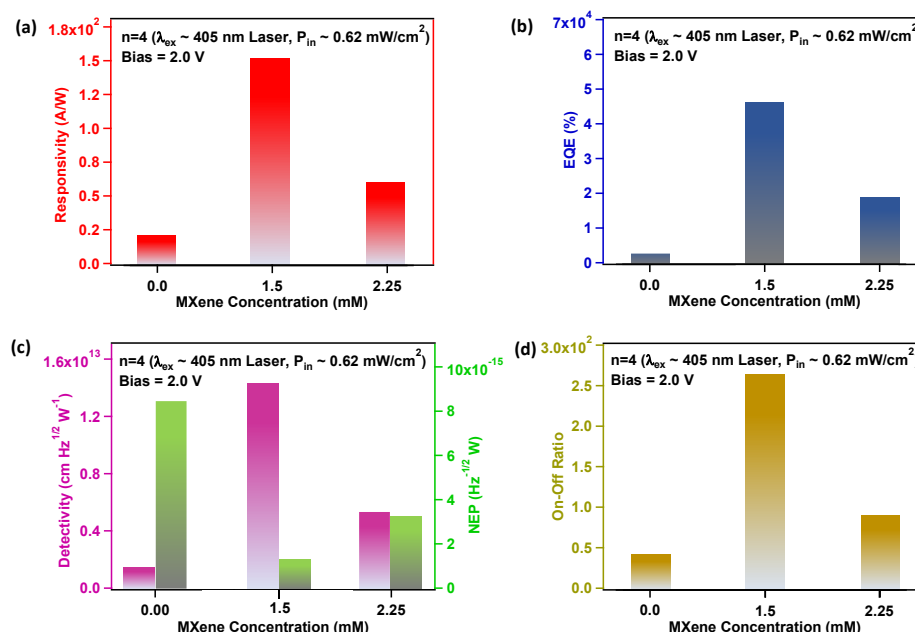


Figure 6.16 Photodetector performance parameters with MXene Concentration: (a) responsivity, (b) EQE (%), (c) detectivity (left axis) and NEP (right axis) and (d) On-Off ratio under the applied bias of 2.0 V. Laser light: $\lambda_{\text{ex}} \sim 405 \text{ nm}$, $P_{\text{in}} \sim 0.62 \text{ mW/cm}^2$ is used for illuminations.

Next, various optoelectronic performance parameters which include ON-OFF ratio, responsivity (R), and external quantum efficiency (EQE), detectivity (D) and noise equivalent power (NEP) for both the pristine and hybrid photodetectors are calculated using the formula mentioned in **Sub-section 2.12.3** of **Chapter 2**. As observed, the hybrid photodetector (n=4 + 1.5 mM MXene) has shown improved $R \sim 1.5 \times 10^2 \text{ A/W}$, $D \sim 14.21 \times 10^{12} \text{ cm Hz}^{1/2}/\text{W}$, $\text{NEP} \sim 1.11 \times 10^{-15} \text{ W/Hz}^{1/2}$, $\text{EQE} (\%) \sim 4.62 \times 10^4$ and ON-OFF Ratio $\sim 2.67 \times 10^2$ at 2.0 V bias under laser illumination ($\lambda_{\text{ex}} \sim 405 \text{ nm}$, $P_{\text{in}} \sim 0.62 \text{ mW/cm}^2$) compare to pristine and hybrid (n=4 + 2.25 mM MXene) based photodetectors. (Figure 6.16a-d). The detailed comparison of these parameters is listed in **Table 6.1**.

Table 6.1 Comparison of optoelectronic parameters for pristine (n=4) and hybrid (n=4 + MXene: 1.5, 2.25 mM) RP Perovskite based photodetectors.

Composition	R (A/W)	D (cm Hz ^{1/2} /W)	EQE %	ON-OFF ratio	NEP (W/Hz ^{1/2})
n=4	18	1.88×10^{12}	0.55×10^4	0.39×10^2	8.41×10^{-15}
n=4+1.50 mM	151	14.21×10^{12}	4.62×10^4	2.67×10^2	1.11×10^{-15}
n=4+2.25 mM	60	5.21×10^{12}	1.84×10^4	0.89×10^2	3.03×10^{-15}

6.7.3 Stability analysis for pristine RP perovskite and perovskite-MXene hybrid thin film based photodetector

Further, to investigate the endurance and stability of pristine and hybrid (n=4 + 1.5 mM MXene) photodetectors, 50 cycle transient photocurrent response is recorded using laser illumination ($\lambda_{\text{ex}} \sim 405 \text{ nm}$, $P_{\text{in}} \sim 0.62 \text{ mW/cm}^2$) at an applied bias of 2.0 V under ambient environment conditions without any encapsulation on the photodetector (see **Sub-Section 2.12.2** in **Chapter 2**). As expected, the hybrid (n=4 + 1.5 mM MXene) photodetector has shown stable performance without

any degradation in peak photocurrent ($I_{\text{light}} = \sim 23.16 \mu\text{A}$ at $t = 0 \text{ sec}$ and $I_{\text{light}} = \sim 23.24 \mu\text{A}$ at $t = 990 \text{ sec}$) after 50 cycles, whereas the pristine photodetector has shown degradation in peak photocurrent by $\sim 34.74 \%$ ($I_{\text{light}} = \sim 2.78 \mu\text{A}$ at $t = 0 \text{ sec}$ and $I_{\text{light}} = \sim 1.81 \mu\text{A}$ at $t = 990 \text{ sec}$) under similar conditions (**Figure 6.17**).

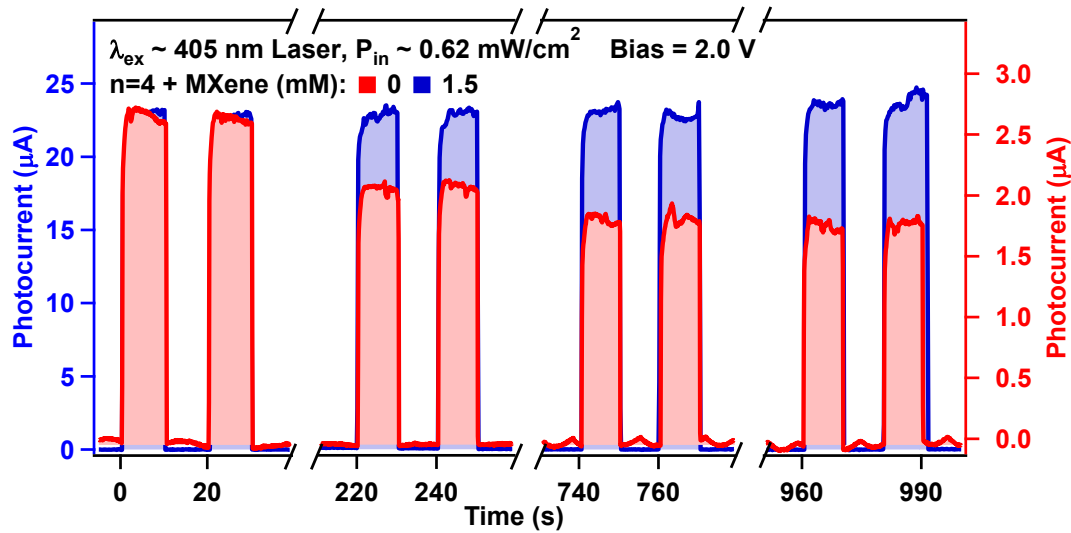


Figure 6.17 50 cycle transient photocurrent response for pristine ($n=4$, right axis) and hybrid ($n=4 + \text{MXene } 1.5 \text{ mM}$, left axis) photodetector at 2.0 V bias.

It must be noted that the optoelectronic performance parameters of demonstrated hybrid ($n=4 + 1.5 \text{ mM MXene}$) photodetector is found to be improved compared to pristine photodetector as well as other solution processed perovskite-based photodetectors, as listed in **Table 6.2**. Such improved optoelectronic performance of the hybrid photodetector with 1.5 mM MXene is attributed to the formation of robust heterointerface between RP perovskite and MXene nanoflakes which has resulted in enhanced crystallinity, improved surface morphology with increase in grain size and reduced pin holes, extraction of photoelectrons as well as least R_{ct} over pristine or hybrid photodetector with 2.25 mM MXene.

6.7.4 I-V characteristics and transient photocurrent measurements for pristine RP perovskite and perovskite-MXene hybrid thin film-based photodetector under variable incident illumination power

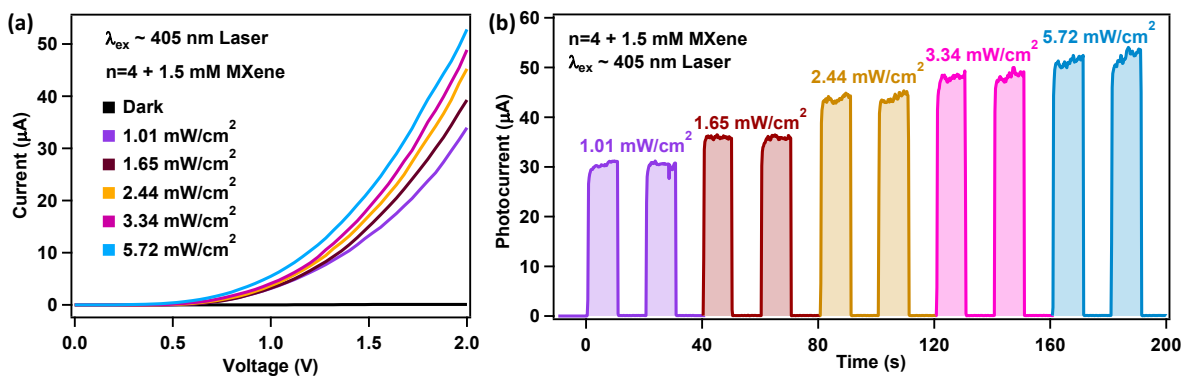


Figure 6.18 (a) Linear I-V characteristics for hybrid ($n=4 + 1.5 \text{ mM MXene}$) photodetector under dark and different illumination power. (b) The transient photocurrent response at 2.0 V bias under different illumination power. All the incident illumination powers are shown in their respective figures.

Further, I-V and I-T characteristics of hybrid ($n=4 + 1.5 \text{ mM MXene}$) photodetector is recorded under high illumination power density of laser ($\lambda_{\text{ex}} \sim 405 \text{ nm}$). As observed, the I-V curves has shown

a uniform enhancement in the photocurrent from ~ 33.96 to ~ 52.81 μA at 2.0 V when incident illumination power density increased from ~ 1.01 to ~ 5.72 mW/cm^2 respectively (**Figure 6.18a**). Furthermore, corresponding similar transient photocurrent response of two cycles at 2.0 V applied bias confirmed the photostability of the device against high incident illumination power (**Figure 6.18b**).

6.7.4.1 Responsivity (R), external quantum efficiency (EQE), detectivity (D) and noise equivalent power (NEP) and ON-OFF ratio for pristine and hybrid photodetector under variable incident illumination power

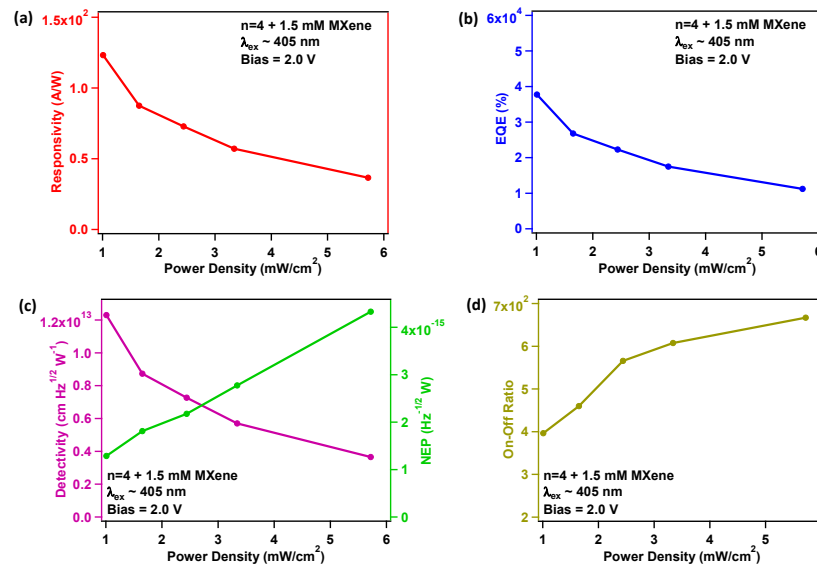


Figure 6.19 Power dependent photodetector performance parameters for hybrid material: (a) responsivity, (b) EQE (%), (c) detectivity (left axis) and NEP (right axis) and (d) On-Off ratio under the applied bias of 2.0 V. Laser light: $\lambda_{\text{ex}} \sim 405$ nm, $P_{\text{in}} \sim 0.62$ mW/cm^2 is used for illuminations.

The range of optoelectronic performance parameters for the hybrid photodetector under varied illumination power density ($1.01 - 5.72$ mW/cm^2) are as follows: $R \sim (1.23 - 0.36) \times 10^2$ A/W , $D \sim (12.30 - 3.65) \times 10^{12}$ $\text{cm Hz}^{1/2}/\text{W}$, $\text{EQE} (\%) \sim (3.77 - 1.12) \times 10^4$, $\text{ON-OFF Ratio} \sim (3.96 - 6.67) \times 10^2$ and $\text{NEP} \sim (1.29 - 4.30) \times 10^{-15}$ $\text{W}/\text{Hz}^{1/2}$ (**Figure 6.19a-d**). The decreased value of R , D , $\text{EQE} (\%)$ as well as increased value of NEP for hybrid ($n=4 + 1.5$ mM MXene) photodetector may be attributed to the increased charge carrier recombination probability in the device under higher optical power.[Behera et al., 2023; Wu et al., 2019] When compared with pristine photodetectors these parameter are still better. For instance, the ON-OFF ratio for hybrid photodetector is enhanced to $\sim 6.67 \times 10^2$ under $P_{\text{in}} \sim 5.72$ mW/cm^2 which is 17 times higher compared to pristine photodetector operated under similar conditions (**Figure 6.16d** & **Figure 6.19d**).

Table 6.2 Comparison of optoelectronic performance parameters for demonstrated $(\text{CH})_2(\text{MA})_3\text{Pb}_4\text{Br}_{13}$ -MXene hybrid photodetector with other recently reported 2D perovskite-based thin film lateral photodetectors.

#	Material	Device Configurations	Bias (V)	R (A/W)	D ($\text{cm Hz}^{1/2}/\text{W}$)	ON-Off ratio	Ref.
1	$(\text{BA})_2(\text{FA})\text{Pb}_2\text{I}_7\text{-Ce}^{3+}$	Au/PSK/Au	2	4.5	4.31×10^{13}	-	[Xian et al., 2023]
2	$(\text{BA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13}$	Au/PSK/Au	20	4.4	5×10^{12}	-	[Li et al., 2023b]
3	$(\text{BA})_2\text{PbI}_4/(\text{BA})_2(\text{MA})\text{Pb}_2\text{I}_7$	Au/PSK/Au	30	8.12	1.5×10^{12}	10^2	[Hwang et al., 2019]
4	$(\text{OA})_2(\text{FA})_{n-1}\text{Pb}_n\text{Br}_{3n+1}$	Au/PSK/Au	9	32	-	-	[Yu et al., 2017]
5	$(\text{PEA})_2(\text{MA})_n$	Au/PSK/Au	9	149	2.0×10^{12}	10^2	[Loi et al.,

	$\text{Pb}_{n+1}\text{I}_{3n+1}/\text{MAPbI}_3$						2020]
6	$(\text{iBA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13}$	Au/PSK/Au	1.5	0.117	-	10^2	[Dong et al., 2018c]
7	$(\text{BA})_2\text{PbI}_4$	Al/PSK/Al	15	0.119	2.15×10^8	-	[Darman et al., 2023]
8	$(\text{PEA})_2(\text{MA})\text{Pb}_2\text{I}_7$	Au/PSK/Au	20	0.012	2.0×10^{11}	10^2	[Chen et al., 2022b]
9	$(\text{PA})_2(\text{FA})\text{Pb}_2\text{I}_7$	Au/PSK/Au	10	-	1.73×10^{14}	10^3	[Han et al., 2019]
10	$(\text{CH})_2(\text{MA})_3\text{Pb}_4\text{Br}_{13}$ -MXene	Al/PSK-MXene/Al	2	151	1.42×10^{13}	10^2	This Chapter

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