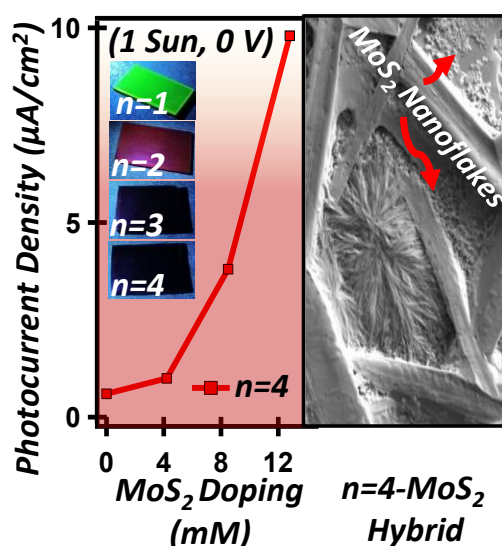


## Strong Photocurrent from Solution Processed Ruddlesden Popper 2D Perovskite-MoS<sub>2</sub> Hybrid Heterojunctions

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This chapter focuses on improving the structural, morphological, optical and optoelectronic properties of RP perovskites of type  $(\text{BA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}$  through the formation of bulk heterojunction with MoS<sub>2</sub> nanoflakes of a few layers. When compared to pristine RP perovskites, RP Perovskite-MoS<sub>2</sub> hybrid thin films show significantly better packing and crystallinity. The addition of MoS<sub>2</sub> in the perovskite layer has enhanced quantum confinement effects and photo-generated charge carrier transport from perovskite to MoS<sub>2</sub>, due to the formation of more number of decay channels and appropriate conduction band of MoS<sub>2</sub>. The optoelectronic properties of RP perovskite-MoS<sub>2</sub> hybrids are investigated with different MoS<sub>2</sub> concentrations (4.2-25.6 mM), and at the optimal concentration (12.8 mM), the photodetectors (n=2, 4) show strong, sharp and highly stable photocurrent response. The RP perovskite (n=4) and MoS<sub>2</sub> (12.8 mM) hybrid-based photodetectors have shown strong photocurrent density of  $\sim 9.8 \mu\text{A}/\text{cm}^2$  under 1 sun illumination when operated at 0.0 V bias conditions without encapsulation, which is  $\sim 17$  times higher as compared to the pristine RP perovskite-based photodetector ( $0.6 \mu\text{A}/\text{cm}^2$ ). Furthermore, hybrid photodetector has shown stable transient photocurrent response with slight reduction of  $\sim 9.6\%$  in peak photocurrent after 200 cycles under photodetector under laser ( $\lambda_{\text{ex}} \sim 405 \text{ nm}$ ,  $\sim 630 \text{ mW}/\text{cm}^2$ ) illumination and without encapsulating the device.

### 3.1 General characteristics of 2D MoS<sub>2</sub> for their potential application in MHP based Optoelectronic devices

Various 3D perovskite-based photodetectors have been demonstrated in the recent past. These devices utilize a variety of 2D inorganic materials, including transition metal dichalcogenides (TMDs) [Kang et al., 2016; Lu et al., 2016a], graphene [Lee et al., 2015; Spina et al., 2015; Sun et al., 2016], reduced graphene oxide (rGO) [He et al., 2015] etc for the purpose of enhancing the extraction of photo-generated charge carriers from the perovskite film. In order to achieve an interface with the perovskite film, various HTMs, including graphene and MoS<sub>2</sub> with a few layers, were integrated into the planar device configuration of these photodetectors. Furthermore, rGO is blended as an ETM with the 3D perovskite [Wang et al., 2017b]. Among many 2D inorganic materials, MoS<sub>2</sub> (mono to few layer) has potential to serve as an ETL [Singh et al., 2019], HTL [Kohnehpoushi et al., 2018] as well as buffer layer (BL) [Liu et al., 2020][Capasso et al., 2016] due to its tunable bandgap from 1.2 to 1.8 eV [Yang et al., n.d.][Steinhoff et al., 2015] which can be achieved by adjusting the number of layers. Moreover few layer MoS<sub>2</sub> offers fast transport of charge carriers in vertical direction [Zhu et al., 2017], fewer traps as it has no dangling bonds on the surface [Singh et al., 2019], high carrier mobility of nearly 500 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> [Huo et al., 2018]. These features provide MoS<sub>2</sub> a promising charge transport material for optoelectronic applications.

Wang et al. (2017) fabricated a 3D perovskite and 2D MoS<sub>2</sub> based photodetector and demonstrated that the ON/OFF ratio of a photodetector can be enhanced through the integration of the 2H phase with the device, in contrast to the 1T phase of 2D MoS<sub>2</sub> [Wang et al., 2017b]. Ranbir et al. carried out an investigation in 2019 on the 3D perovskite MAPbI<sub>3</sub> solar cell, which featured CVD-grown MoS<sub>2</sub> as the ETL and Spiro-OMeTAD as the HTL. The authors reported a PCE of 13.2%, which was comparable to the PCEs achieved from SnO<sub>2</sub> and compact TiO<sub>2</sub> ETL-based PSCs [Singh et al., 2019]. This was attributed to the broad transmission in the visible spectrum from 400-780 nm, [Hashemi et al., 2022] absorption efficiencies exceeding 77% and a maximum of 88% of MoS<sub>2</sub> [Singh et al., 2019]. In 2020, Zhiyong et al. conducted an investigation into the power conversion efficiency (PCE) of solar cell utilizing MoS<sub>2</sub> as both an additive and buffer layer (BL) between PEDOT:PSS and perovskite. This BL restricts the degradation of perovskite film from acidic PEDOT:PSS films. The active layer of MAPbI<sub>3</sub>:MoS<sub>2</sub> (10 v%) and bi-layer MoS<sub>2</sub> as BL resulted in a 12% increase in PCE from 15.29% to 18.31% of PSC. Additionally, 87% of the initial PCE was maintained after 20 days [Liu et al., 2020]. Saman et al. in 2018 examined the PCE of a 3D perovskite MAPbI<sub>3</sub>-based solar cell with a varying thickness of MoS<sub>2</sub> and serving as HTL. As the thickness of the MoS<sub>2</sub> film increases, the PCE increases, reaching 20.53% for a 1.34 nm thick film. However, the PCE decreases to 16.21% as the MoS<sub>2</sub> film thickness increases to 21.44 nm. This decrease in PCE was due to the increased resistance in the device as a result of the multilayer MoS<sub>2</sub> and lower transmission of light through MoS<sub>2</sub> [Kohnehpoushi et al., 2018]. These recent reports demonstrate that monolayer as well as few layer MoS<sub>2</sub> can be a promising additive, buffer layer as well as charge transport inorganic material which can efficiently improve the performance of perovskite-based optoelectronics due to their suitable band alignment with perovskite, improved interface area for better charge transport and can offer a stable heterojunction, solvent compatibility etc. Still, the effect of these TMDs is not investigated on the performance of RP perovskite based optoelectronic devices, which is rather crucial to attain stable and effective functioning of such devices.

### 3.2 Brief discussions on the synthesis procedure of RP perovskite (BA)<sub>2</sub>(MA)<sub>n-1</sub>PbI<sub>3n+1</sub> (n=1-4) and few layer of MoS<sub>2</sub> nanoflakes

The synthesis of RP perovskite materials (BA)<sub>2</sub>(MA)<sub>n-1</sub>PbI<sub>3n+1</sub> (n = 1-4) is synthesized by adopting already reported synthesis route. Where, HI and H<sub>3</sub>PO<sub>2</sub> act as reaction medium and reducing agent respectively. Moreover, PbO, BA and MA serve as precursors. The molar ratio of BA, MA, and H<sub>3</sub>PO<sub>2</sub> is adjusted to control the number of inorganic octahedra layers which is denoted by the n-value during synthesis process (see Section 2.1.2 in Chapter 2 for more details). The schematic for the crystal structure of RP perovskite (BA)<sub>2</sub>(MA)<sub>n-1</sub>PbI<sub>3n+1</sub> (n=1-4) are depicted in Figure 3.1a. The n-value determines the number of inorganic metal halide octahedra [PbI<sub>6</sub>]<sup>4-</sup> layers. During the self-assembling process, organic spacer cations BA are sandwiched between octahedra of varying

thickness by weak intermolecular interactions and hydrophobic forces, while MA cations are caged in between the octahedrons, resulting in an orthorhombic crystal structure [Stoumpos et al., 2016].

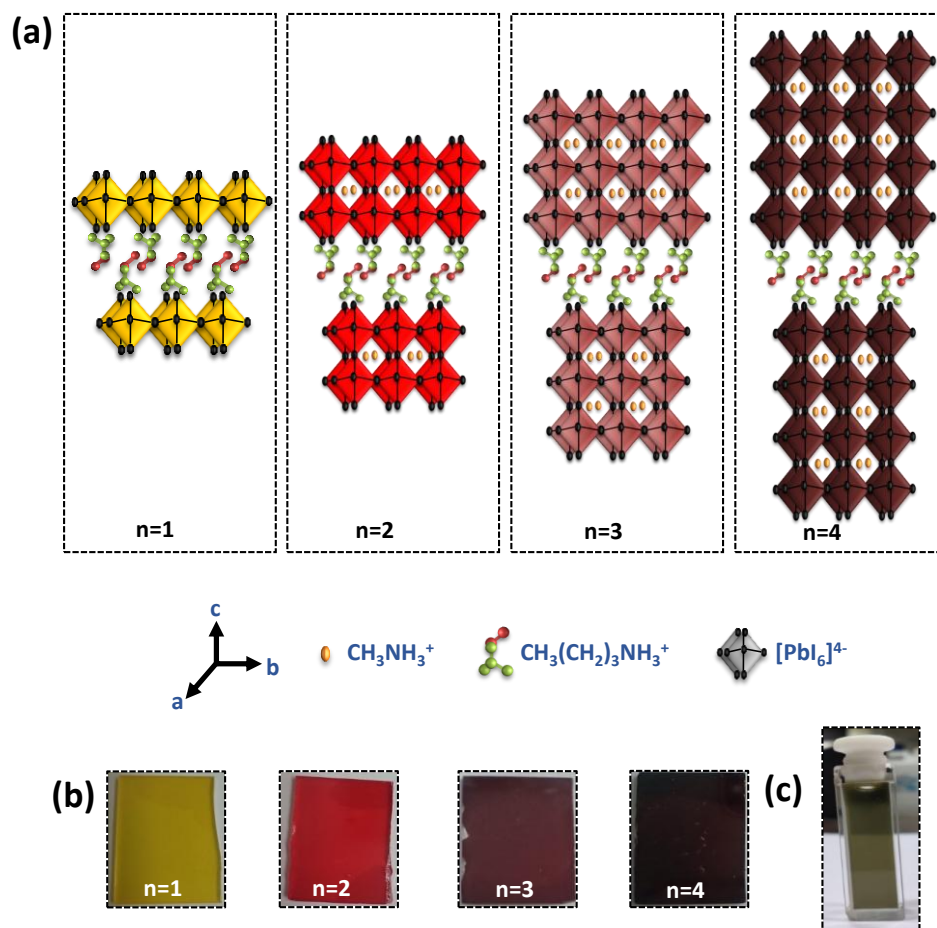


**Figure 3.1** (a) Schematic illustration of the crystal structure of  $(\text{BA})_2(\text{MA})_{n-1}\text{PbIn}_{3n+1}$  ( $n = 1-4$ ) and (b) the corresponding digital camera image of thin films. (c) shows the digital camera image of  $\text{MoS}_2$  dispersion prepared by LPET in NMP.

These organic-inorganic layers are alternatively stacked and confined, which enables the dielectric and quantum confinement effects. This results in unique optical and structural properties, [Zhou et al., 2016] which are further discussed below. Moreover, the optical band tunability of the pristine RP perovskite spin-coated thin film can be observed in digital camera images (**Figure 3.1b**), ranging from yellow ( $n=1$ ) to black ( $n=4$ ). A steady  $\text{MoS}_2$  suspension is synthesized from their bulk  $\text{MoS}_2$  particles by employing LPET in NMP (**Figure 3.1c & see Section 2.2 in Chapter 2 for more details**), as the surface tension of NMP at around  $40 \text{ mJ/m}^2$  is in close alignment with the surface energy of many layered materials [Sahoo et al., 2020][Gupta et al., 2016][Cunningham et al., 2012]. Additionally, LPET is a technique that is cost-effective, environmentally friendly, and free of contamination for the synthesis of  $\text{MoS}_2$  suspension.

### 3.3 Brief discussions on the fabrication of RP perovskite- $\text{MoS}_2$ hybrids

The RP perovskite- $\text{MoS}_2$  hybrid solution for  $n = 1$  to 4 is produced by combining its 0.5 M molar mass (which corresponds to 25.9 mg for  $n=1$ , 44.4 mg for  $n=2$ , 63.0 mg for  $n=3$ , and 81.6 mg for  $n=4$ ) with a  $60 \mu\text{l}$   $\text{MoS}_2$  solution that contains six distinct millimolar concentrations: 4.2 mM, 8.5 mM, 12.8 mM, 17.0 mM, 21.3 mM, and 25.6 mM. The hybrid solution is then uniformly prepared through ultrasonication and followed by stirring. Since the size of synthesized  $\text{MoS}_2$  nanoflakes vary from 30 to 200 nm (**as discussed below in morphology section 3.5.1.**). Therefore it is anticipated that when the solution of hybrids are casted over substrate, then RP perovskite crystals undergo heterogeneous

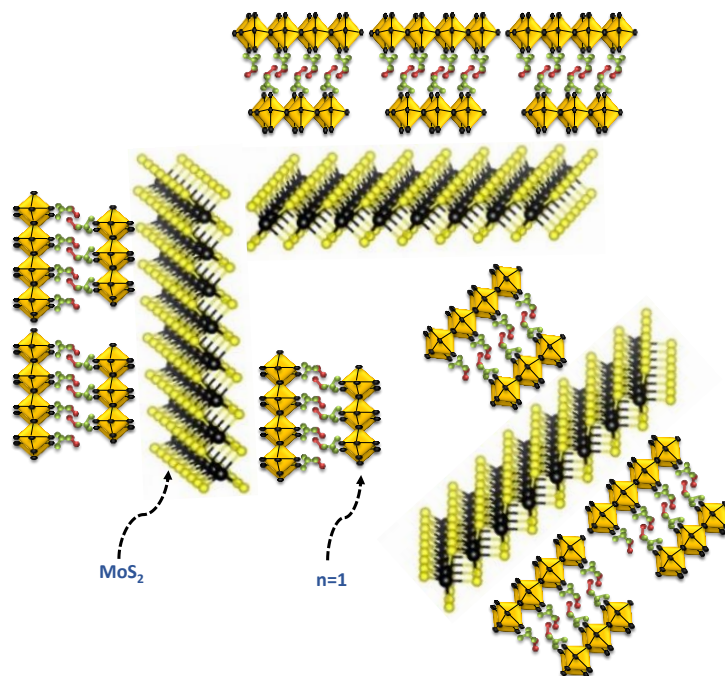


**Figure 3.2** Schematic illustration of  $(\text{BA})_2\text{PbI}_4$  perovskite crystals assembled on  $\text{MoS}_2$  to form heterostructure.

nucleation during crystallization process [Liu et al., 2020]. This process is triggered by the presence of  $\text{MoS}_2$  heterogeneous phase in perovskite precursors, as depicted in the close view diagram (**Figure 3.2**). The thin film and dropcasted preparation method is mentioned in Sub-Section 2.5.1 of Chapter 2.

### 3.4 Structural properties

#### 3.4.1 Crystal structure for RP perovskite and RP perovskite- $\text{MoS}_2$ hybrids

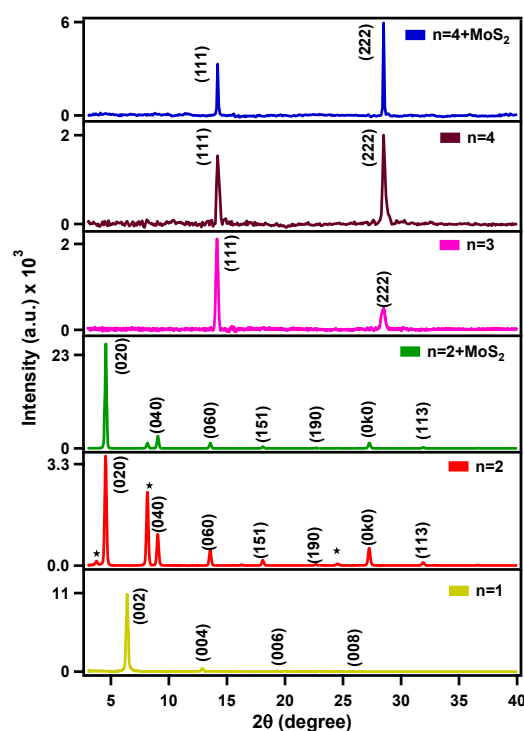


**Figure 3.3** XRD patterns of pristine  $(\text{BA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$  ( $n = 1-4$ ) spin coated thin films and  $(\text{BA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$  ( $n=2$  and  $4$ )+ $\text{MoS}_2$  (12.8 mM) hybrid spin coated thin films. All the films are fabricated on the glass substrate.

In order to understand the crystal structures of these RP perovskite materials and RP perovskite-MoS<sub>2</sub> hybrids, thin film XRD measurements have been performed. The highly crystalline nature of the films is confirmed by the XRD plots of RP perovskite materials and RP perovskite-MoS<sub>2</sub> hybrid thin films (**Figure 3.3**). The crystal structure of  $n=1$  indicates that these pure 2D materials have a tendency to develop perpendicular to the substrate, specifically along the  $c$ -axis. Consequently, they exhibit characteristic (00l)-type reflections [Zhou et al., 2016]. The  $n=2$  RP perovskite is the consequence of a change in the stoichiometric formula and the inclusion of MA cations. The MA cations were caged between octahedron layers, as evidenced by the presence of (151), (190), and (113) reflections. These reflections demonstrates the progressive expansion of unit cell along the  $c$ -axis [Zhou et al., 2016]. Moreover, RP perovskite with  $n = 3$  and  $n = 4$ , indicates two XRD peaks which correspond to the (111) and (222) reflections, which has resulted in the presence of 3D perovskite phase within the RP perovskite material (**Figure 3.3**). In the XRD plots of hybrid thin films composed of  $(\text{BA})_2(\text{MA})_{n-1}\text{Pb}_{n-1}\text{I}_{3n+1}$  ( $n = 2$  and  $4$ ) + MoS<sub>2</sub> (12.8 mM), it was observed that the plane diffraction angles of the RP perovskite did not undergo any changes as a result of the presence of MoS<sub>2</sub>. Furthermore, a significant increase in the intensity of reflected X-rays has been detected, which demonstrates that the presence of MoS<sub>2</sub> has greatly increased the crystallinity of RP perovskites [Liu et al., 2020]. The reason for this is that the presence of MoS<sub>2</sub> enhances the packing of the perovskite crystals. This is due to the heterogeneous nucleation of perovskite, which is induced by the existence of a heterogeneous MoS<sub>2</sub> phase in the perovskite precursors. This phase has the ability to promote crystallization during the annealing process, which takes place at a temperature of 100 °C [Liu et al., 2020],[Yan et al., 2015].

### 3.4.2 Crystal structure for MoS<sub>2</sub> and exfoliated MoS<sub>2</sub> nanoflakes

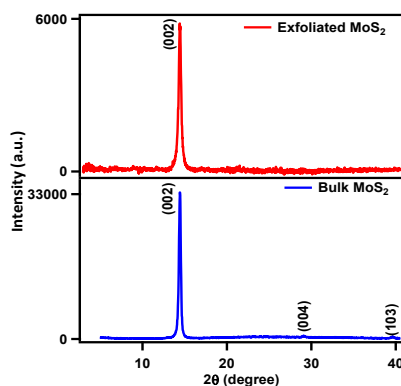


**Figure 3.4** X-ray diffraction pattern of drop coated films of exfoliated MoS<sub>2</sub> nanoflakes (top) and bulk MoS<sub>2</sub> (bottom).

XRD plots of the MoS<sub>2</sub> nanoflakes drop-casted film revealed an increased FWHM and a decreased intensity for the characteristic (002) peak, confirming the presence of few-layer MoS<sub>2</sub> (**Figure 3.4**) [Sahoo et al., 2020]. Additionally, the 2H phase (trigonal prismatic coordinated crystal structure) of MoS<sub>2</sub> [Yu et al., 2018] was confirmed by the characteristic (002) peak at 14.4°. This phase is well-suited for optoelectronic applications due to its semiconducting nature [Lee et al., 2012],[Majee et al., 2019],[Kim et al., 2020b],[Yin et al., 2012].

## 3.5 Morphological properties

### 3.5.1 Surface morphology for dropcasted exfoliated MoS<sub>2</sub> nanoflake

The surface morphology and size of MoS<sub>2</sub> were examined by FESEM (**Figure 3.5a**). The results shows that the bulk MoS<sub>2</sub> flakes, which have in micron size before exfoliation, [Dong et al., 2016] were reduced to nanoflake structures with an average size of around 60 nm. Furthermore, the number of MoS<sub>2</sub> atomic layers in the nanoflakes may be determined using AFM by measuring the height of the nanostructures on a glass substrate (**Figure 3.5b**).

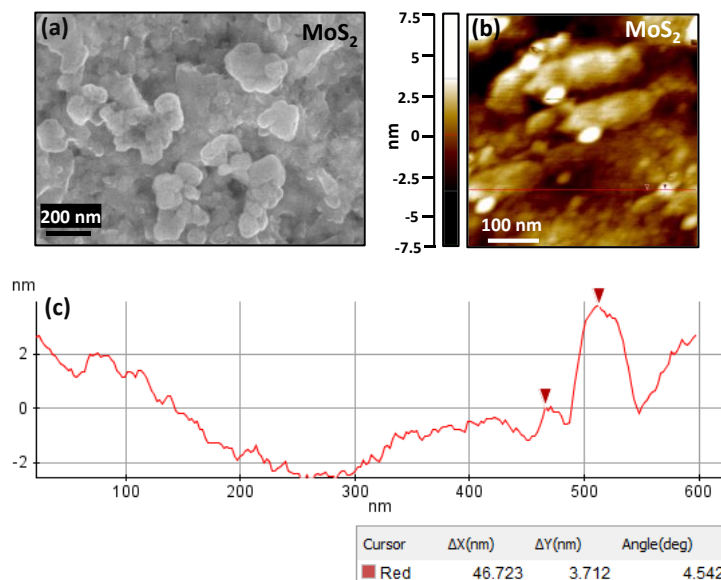


**Figure 3.5** Top view (a) FESEM image and (b) atomic force microscope (AFM) plot of exfoliated MoS<sub>2</sub>, and corresponding (c) line profile to estimate the number of atomic layers.

Furthermore, AFM line profile measurements showed that the height of MoS<sub>2</sub> is around 3.712 nm, which is equivalent to 5 atomic layers of MoS<sub>2</sub> (assuming each layer is 0.65 nm thick) as shown in **Figure 3.5c** [Splendiani et al., 2010] [Li et al., 2015].

### 3.5.2 Surface morphology for spin coated RP perovskite and RP perovskite-MoS<sub>2</sub> hybrid films

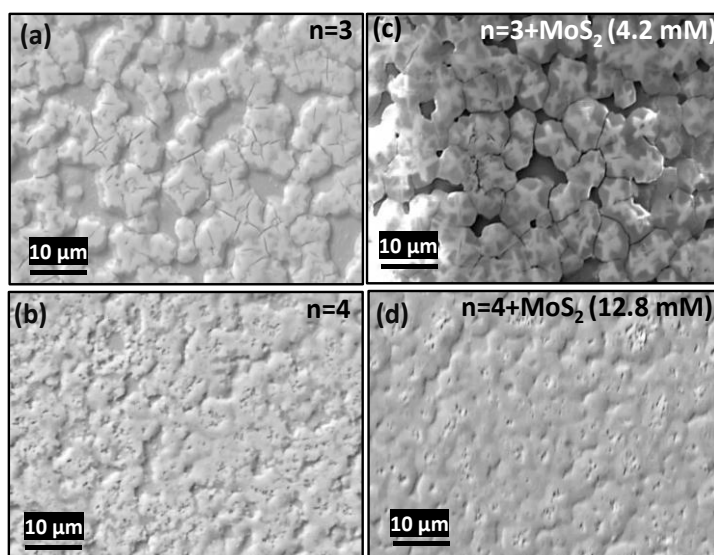


**Figure 3.6.** Top view SEM images for the spin coated thin films of (a) RP perovskite (BA)<sub>2</sub>(MA)<sub>2</sub>Pb<sub>3</sub>I<sub>10</sub>, n=3 and (b) RP perovskite (BA)<sub>2</sub>(MA)<sub>3</sub>Pb<sub>4</sub>I<sub>13</sub>, n=4 (c) RP perovskite (BA)<sub>2</sub>(MA)<sub>2</sub>Pb<sub>3</sub>I<sub>10</sub>+MoS<sub>2</sub> hybrid. (d) RP perovskite (BA)<sub>2</sub>(MA)<sub>3</sub>Pb<sub>4</sub>I<sub>13</sub>+MoS<sub>2</sub> hybrid.

The top view SEM imaging is performed for pristine RP perovskite and their hybrid thin films to investigate the effect of MoS<sub>2</sub>. Pristine n=3 perovskite thin film has shown non-uniform and irregular growth of perovskite crystals. Whereas there is a large number of pin holes available in n=4 perovskite crystals (**Figure 3.6a-b**). On the counterpart, the hybrid thin films composed of RP perovskite and MoS<sub>2</sub> were enhanced their morphology by a substantial decrease in pin holes and an improvement in perovskite film coverage when MoS<sub>2</sub> was present in RP perovskite thin films (n=3 and 4, respectively) at concentrations of 4.2 and 12.8 mM, respectively (**Figure 3.6c-d**).

### 3.5.3 Surface morphology for the dropcasted RP perovskite and RP perovskite-MoS<sub>2</sub> hybrid film

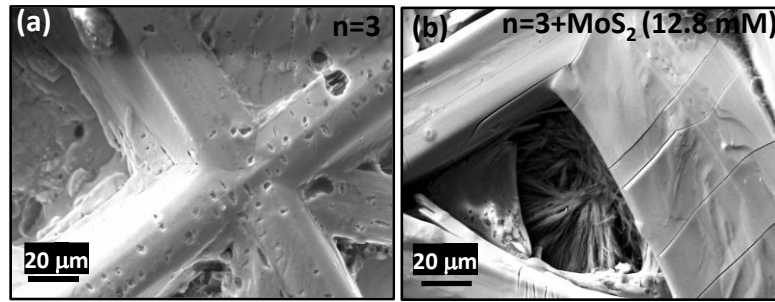


**Figure 3.7** Top view SEM images for the drop casted films of (a) RP perovskite (BA)<sub>2</sub>(MA)<sub>2</sub>Pb<sub>3</sub>I<sub>10</sub>, n=3 and (b) RP perovskite (BA)<sub>2</sub>(MA)<sub>2</sub>Pb<sub>3</sub>I<sub>10</sub>+MoS<sub>2</sub> hybrid.

In addition, SEM imaging for the pristine and hybrid dropcasted film of n=3 RP perovskites are also performed to investigate the effect of MoS<sub>2</sub> (**Figure 3.7**). As expected, hybrid film has shown improved morphology with obvious no pin holes. The improvement in morphology of perovskite-MoS<sub>2</sub> thin/dropcasted film and reduction in the pin holes is due to the heterogeneous nucleation of perovskite crystals, which is caused by the presence of MoS<sub>2</sub> as discussed earlier. These enhanced morphologies and high crystallinities of the perovskite-MoS<sub>2</sub> hybrids may lead to increased light absorption, decreased defects and series resistance, and decreased trap-assisted recombination, which ultimately results in a considerable improvement in the device's performance [Zhou et al., 2016]. It has been determined that the heterogeneous nucleation of perovskite crystals, which is caused by the presence of MoS<sub>2</sub>, is responsible for the observed improvement in perovskite-MoS<sub>2</sub> film shape and the reduction in pin holes. This was described in item [Liu et al., 2020]. The formation of a type-II (staggered) semiconductor heterojunction is the consequence of the interface between perovskite crystals and MoS<sub>2</sub>, as can be seen in the schematic depiction of **Figure 3.2**.

### 3.5.4 Elemental Composition for perovskite-MoS<sub>2</sub> hybrids

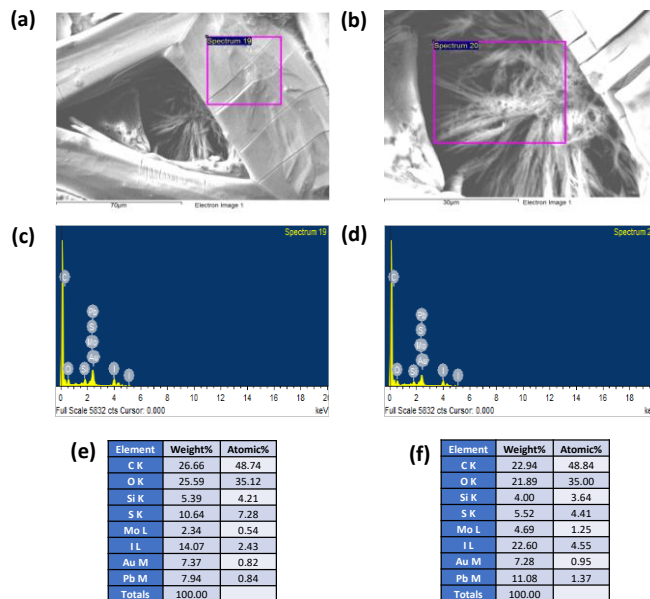


**Figure 3.8** (a,b) SEM images for the RP perovskite (BA)<sub>2</sub>(MA)<sub>2</sub>Pb<sub>3</sub>I<sub>10</sub> (n=3)+MoS<sub>2</sub> (12.8 mM) hybrid drop casted film taken at different locations on the film to get the energy dispersive analysis (EDAX) data corresponding to the scanned area shown by pink color square box. (c) and (d) shows the corresponding EDAX spectra of hybrid films obtained for the scanned area shown in figure (a) and (b) respectively. (e) and (f) shows the corresponding weight/atomic percentage of hybrid films obtained from the EDAX spectra shown in figure (c) and (d) respectively.

The EDAX analysis was used to verify the elemental composition of the hybrid,  $n=3+\text{MoS}_2$  (12.8 mM) drop casted film as well as the spatial distribution of the elements. The corresponding elemental composition spectra and mapping provide evidence that the film contains carbon, iodine, lead, molybdenum, and sulfur, all of which are dispersed in a uniform manner over its surface (**Figure 3.8a-f**).

## 3.6 Optical properties

### 3.6.1 Absorbance spectra for RP perovskite and RP Perovskite- $\text{MoS}_2$ hybrids

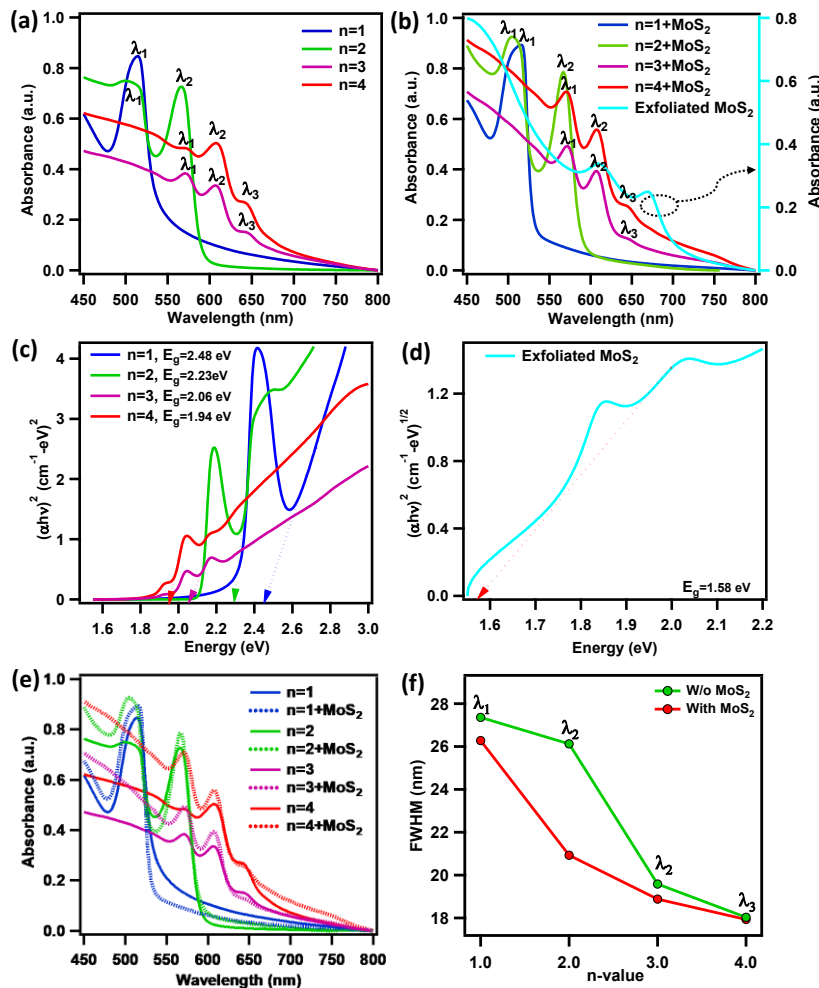


**Figure 3.9** Room-temperature optical absorption spectrum of (a)  $(\text{BA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}$  ( $n=1-4$ ) and (b)  $(\text{BA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}+\text{MoS}_2$  (12.8 mM) thin films. Bandgap calculations using Tauc's Plot of pristine (c)  $(\text{BA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}$  ( $n=1-4$ ) and (d) exfoliated  $\text{MoS}_2$  thin films. (e) Room-temperature optical absorption spectrum of  $(\text{BA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}$  ( $n=1-4$ ) and respective  $\text{MoS}_2$  hybrid thin films to compare the absorbance. (f) Variation of FWHM as a function of  $n$ -value for  $(\text{BA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}$  ( $n=1-4$ ) and  $(\text{BA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}+\text{MoS}_2$  (12.8 mM) thin films.

The investigations of the thin film optical absorbance of pure as well as  $\text{MoS}_2$  doped RP perovskite have shown high exciton absorption peaks and uniform band gap tunability in the visible region of spectra, with the range of wavelengths extending from 513 nm for  $n=1$  to 644 nm for  $n=4$  (**Figure 3.9a,b**). The appearance of several exciton peaks for  $n=2-4$  indicate the occurrence of mixed phases [Dong et al., 2018b][Zhao et al., 2016a]. However their optical band gaps are determined using Tauc's Plot for the characteristic absorption peaks at 513 nm ( $\lambda_1$  for  $n=1$ ), 567 nm ( $\lambda_2$  for  $n=2$ ), 607 nm ( $\lambda_2$  for  $n=3$ ), and 644 nm ( $\lambda_3$  for  $n=4$ ) and demonstrated decrease in energy band gap ranging from 2.48 eV to 1.93 eV respectively (**Figure 3.9c**). Furthermore, the absorbance of  $\text{MoS}_2$  is obtained on a drop-cast film to further verify the existence of few-layer  $\text{MoS}_2$ . The presence of peaks between

600 and 700 nm indicated the existence of a 2H phase, which has semiconducting properties. The peaks are attributed to A and B excitons obtained from the K point of the Brillouin zone, which are responsible for the semiconducting behavior [Wang et al., 2017b][Wang et al., 2013]. The peculiar absorption peak at 669 nm confirms the existence of few-layer MoS<sub>2</sub>, corresponding with an optical band gap of 1.58 eV (**Figure 3.9d**). The absorbance spectra of (BA)<sub>2</sub>(MA)<sub>n-1</sub>PbI<sub>3n+1</sub> (n=1-4) + MoS<sub>2</sub> (12.8 mM) hybrid thin films indicate that the exciton absorption peaks increased and narrowed, without any shift in peak wavelengths. This phenomenon corresponds to enhanced light absorption resulting from improved surface morphology and crystallinity of the perovskite films (**Figure 3.9e**) [Singh et al., 2019]. The FWHM values for (BA)<sub>2</sub>(MA)<sub>n-1</sub>PbI<sub>3n+1</sub> (n=1-4) are 27.37 nm, 26.13 nm, 19.58 nm, and 18.03 nm, respectively, whereas the values for (BA)<sub>2</sub>(MA)<sub>n-1</sub>PbI<sub>3n+1</sub> (n=1-4)+MoS<sub>2</sub> hybrids are 26.28 nm, 20.93 nm, 18.89 nm, and 17.93 nm (**Figure 3.9f**). The lowered FWHM of the MoS<sub>2</sub> added perovskite film demonstrates that the confinement effects are more prominent as a result of the superior stacking of organic and inorganic layers [Li et al., 2021a][Liu et al., 2019].

### 3.6.2 PL and lifetime spectra for RP perovskite and RP perovskite-MoS<sub>2</sub> hybrids

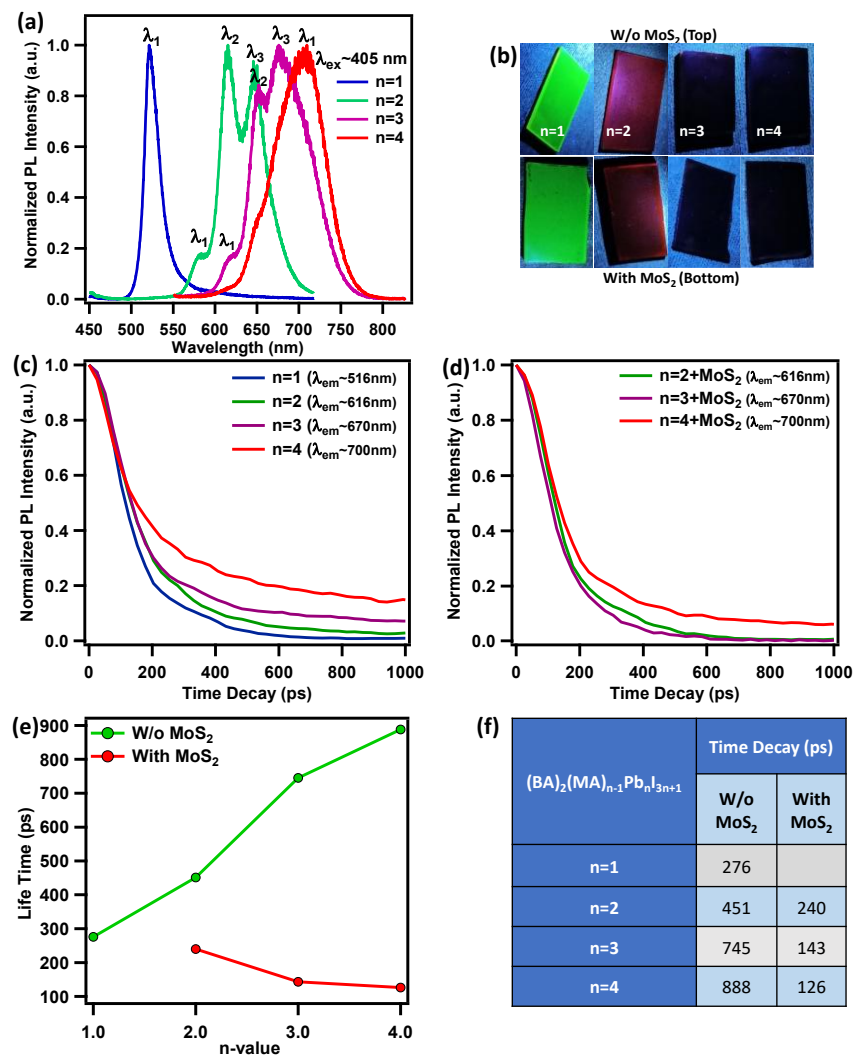


**Figure 3.10** (a) PL spectrum of (BA)<sub>2</sub>(MA)<sub>n-1</sub>PbI<sub>3n+1</sub> (n = 1-4) thin films (λ<sub>ex</sub> = 405nm laser, 10 μm beam spot size), (b) PL images of (BA)<sub>2</sub>(MA)<sub>n-1</sub>PbI<sub>3n+1</sub> (n=1-4) and (BA)<sub>2</sub>(MA)<sub>n-1</sub>PbI<sub>3n+1</sub> (n = 1-4) + MoS<sub>2</sub> (12.8 mM) thin film under UV excitation (λ<sub>ex</sub> ~300 nm LED) without using any long pass filter. PL decay lifetimes obtained for (c) pristine (BA)<sub>2</sub>(MA)<sub>n-1</sub>PbI<sub>3n+1</sub> (n = 1-4) and (d) (BA)<sub>2</sub>(MA)<sub>n-1</sub>PbI<sub>3n+1</sub> (n = 2-4) + MoS<sub>2</sub> (12.8 mM) hybrid thin films using time-resolved PL spectroscopy. (e) Variation of PL decay life times as a function of n-value for (BA)<sub>2</sub>(MA)<sub>n-1</sub>PbI<sub>3n+1</sub> (n = 1-4) and (BA)<sub>2</sub>(MA)<sub>n-1</sub>PbI<sub>3n+1</sub> (n = 2-4)+MoS<sub>2</sub> (12.8 mM) hybrid thin films. (f) Shows the corresponding PL decay lifetimes obtained after double exponential curve fitting.

The PL measurements of pristine  $(\text{BA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}$  ( $n=1-4$ ) thin films exhibit high exciton emission peaks at 513 nm ( $\lambda_1$  for  $n=1$ ), 571 nm ( $\lambda_2$  for  $n=2$ ), 607 nm ( $\lambda_2$  for  $n=3$ ), and 644 nm ( $\lambda_3$  for  $n=4$ ). These measurements were carried out in reflection mode under a laser excitation having wavelength of 405 nm (beam spot size  $\sim 10 \mu\text{m}$ ) (**Figure 3.10a**). It has been determined that the existence of mixed phase of RP perovskite is responsible for the formation of extra emission peaks for  $n=2-4$  emission peaks [Dong et al., 2018b]. Further to confirm the PL quenching effect, PL camera imaging are carried out for pristine and hybrid thin films under UV LED illumination with an excitation wavelength of 300 nm (without any long pass filter) as shown in **Figure 3.10b**. The quenched PL in perovskite-MoS<sub>2</sub> hybrids result from the transport of electrons from RP perovskite to MoS<sub>2</sub> which has valence band maxima (VBM) of around 5.58 eV and conduction band minima (CBM) of around 4.00 eV. This improved photo-generated electron from perovskites decreased the radiative loss. To fully understand how MoS<sub>2</sub> enhances the charge transport characteristics of RP perovskite films, more studies such micro-confocal PL and impedance spectroscopy are recommended.

**Table 3.1** Room-Temperature exciton absorption peak wavelength  $\lambda_{\text{abs}}$  (nm) and corresponding energy  $E_{\text{abs}}$  (eV), exciton PL peak wavelength  $\lambda_{\text{PL}}$  (nm) and corresponding energy  $E_{\text{PL}}$  (eV), Stokes shift (meV), energy band gap (eV), exciton binding energy  $E_{\text{B.E.}}$  (meV) and life time (ps) for  $(\text{BA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}$  ( $n = 1-4$ ) thin films.

| $(\text{BA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}$         | Abs Peak $\lambda_{\text{abs}}$ (nm) | $E_{\text{abs}}$ (eV) | PL Peak $\lambda_{\text{PL}}$ (nm) | $E_{\text{PL}}$ (eV) | Stokes Shift (nm) | Stokes Shift $\Delta E = E_{\text{abs}} - E_{\text{PL}}$ (meV) | $E_{\text{g}}$ (eV) | Exciton Binding Energy $E_{\text{B.E.}} = E_{\text{g}} - E_{\text{abs}}$ (meV) | Life Time (ps) |
|-----------------------------------------------------------|--------------------------------------|-----------------------|------------------------------------|----------------------|-------------------|----------------------------------------------------------------|---------------------|--------------------------------------------------------------------------------|----------------|
| $n=1, (\text{BA})_2\text{PbI}_4$                          | 513 ( $\lambda_1$ )                  | 2.42                  | 521 ( $\lambda_1$ )                | 2.38                 | 8                 | 40                                                             | 2.48                | 70                                                                             | 276            |
| $n=2, (\text{BA})_2(\text{MA})_1\text{Pb}_2\text{I}_7$    | 567 ( $\lambda_2$ )                  | 2.19                  | 615 ( $\lambda_2$ )                | 2.02                 | 44                | 150                                                            | 2.23                | 40                                                                             | 451            |
| $n=3, (\text{BA})_2(\text{MA})_2\text{Pb}_3\text{I}_{10}$ | 607 ( $\lambda_2$ )                  | 2.04                  | 675 ( $\lambda_3$ )                | 1.84                 | 68                | 200                                                            | 2.06                | 20                                                                             | 745            |
| $n=4, (\text{BA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13}$ | 644 ( $\lambda_3$ )                  | 1.93                  | 708 ( $\lambda_1$ )                | 1.75                 | 68                | 190                                                            | 1.94                | 10                                                                             | 888            |

TRPL measurements are carried out using a TCSPC setup with a 405 nm pulsed diode laser in order to get better understanding of the kinetics of exciton recombination in both pristine and hybrid thin films. For these measurements samples are prepared on a glass substrate. The lifetimes of photogenerated charge carriers are recorded for the characteristic wavelengths (**Table 3.1**) and determined using double exponential fitting of decay profile (**Figure 3.10c,d**) [Rahil et al., 2022a]. It has been shown that the charge carrier lives of pristine perovskite films rise linearly from 276 picoseconds for  $n=1$  to 888 picoseconds for  $n=4$  (**Figure 3.10e,f**). On the other hand, the lifetimes of MoS<sub>2</sub>-doped perovskite films drop linearly from 240 picoseconds for  $n=2$  to 126 picoseconds for  $n=4$  (**Figure 3.10e,f**). The observed decrease in the average lifespan of hybrid films is because of the fact that when the perovskite band gap decreases with increasing  $n$ -value, the VBM and CBM alignment of the hybrid films with MoS<sub>2</sub> improves. This, in turn, leads to the efficient dissociation of e-h pairs at the heterojunction between the perovskite and MoS<sub>2</sub>. The formation of additional decay channels is a consequence of this e-h pair dissociation, which is caused by the effective transport of electrons from perovskite to MoS<sub>2</sub> ( $n=1-4$ ), while simultaneously blocking holes [Singh et al., 2019]. As a result, these hybrids have the potential to be investigated for use in fast response optoelectronics, such as photodetectors.

## 3.7 Optoelectronic properties

### 3.7.1 Energy band diagram for RP perovskite and MoS<sub>2</sub>

In order to examine the effect of the addition of MoS<sub>2</sub> on the optoelectronic properties of RP perovskites, photocurrent studies are carried out on pristine RP perovskite and MoS<sub>2</sub> doped RP perovskite thin films. This is achieved by fabricating the vertical configuration photodetector on

patterned FTO substrates, which are referred to as  $(\text{FTO}/(\text{BA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}-\text{MoS}_2/\text{Al})$  (see Sub-Section 2.7.1 and Sub-Section 2.5.2 in Chapter 2).

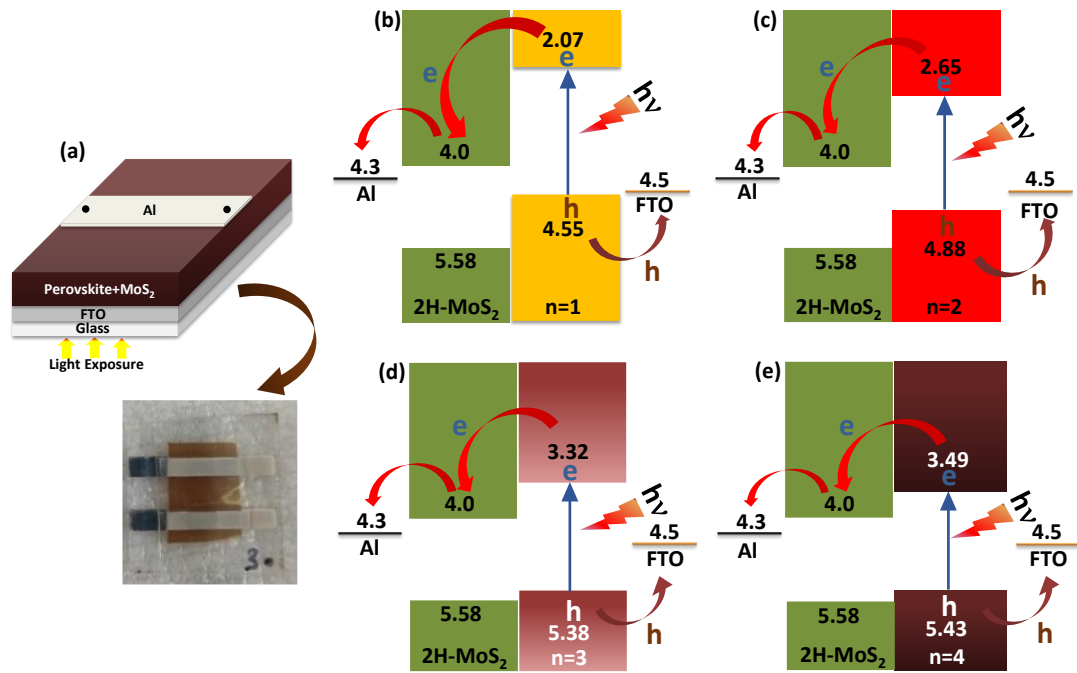


**Figure 3.11** (a) Schematic illustration of vertical two electrode based photodetector for the hybrid of  $(\text{BA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}$  ( $n=1-4$ )+MoS<sub>2</sub> hybrids under the exposure of Xenon lamp along with the digital camera image of actual device (right side). (b) Schematic illustration of energy bands showing the charge transport mechanism occurring in  $(\text{BA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}$  ( $n=4$ )+MoS<sub>2</sub> hybrid photodetector.

The schematic diagram for demonstrated photodetector is shown in **Figure 3.11a**. The value of VBM and CBM of  $(\text{BA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}$  ( $n=1-4$ ) both shift to higher energies as the  $n$ -value increases, as has been observed in other reports [Cao et al., 2015][Tsai et al., 2016b][Cao et al., 2015]. Moreover, MoS<sub>2</sub> exhibits VBM of 5.58 eV and CBM of 4.0 eV (**Figure 3.11b-e**). Therefore acting as ETM for  $(\text{BA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}$  ( $n=1-4$ ) [Singh et al., 2019][Wang et al., 2017c]. Under illumination, electron-hole pairs are generated in RP perovskite material. These electron hole pairs are separated due to internally generated field which has resulted in transport of electron from the conduction band of RP perovskite to MoS<sub>2</sub>, leaving holes in the valence band. Further, these electrons and holes has transported and collected to the corresponding electrode which are Al and FTO as demonstrated in the **figure 3.11b-e**.

### 3.7.2 J-V characteristics for RP perovskite and RP perovskite-MoS<sub>2</sub> hybrids

Further, the J-V characteristics are investigated from -1.0 V to +1.0 V under dark and illumination conditions for pristine RP perovskite thin film  $(\text{BA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}$  ( $n=1-4$ ) and their corresponding hybrids, where the concentration of MoS<sub>2</sub> nanoflakes is 12.8 mM. It is observed that the films exhibit a diode-like behavior, which is a confirmation of their semiconducting nature (**Figure 3.12a-d**). Furthermore, when the films were illuminated with standard 1 sun light (with AM1.5 filter), an increase in photocurrent was observed due to the generation of electron hole pairs. In the case of RP perovskite  $(\text{BA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}$  ( $n=1-4$ )+MoS<sub>2</sub> (12.8 mM) hybrid thin films, it is observed that the photocurrent was significantly higher as compare to pristine counterpart. This confirms that the MoS<sub>2</sub> is functioning effectively as an ETM for the  $(\text{BA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}$  ( $n=1-4$ ) hybrid thin films, without changing the intrinsic semiconducting nature of RP perovskite material (**Figure 3.12a-d**).

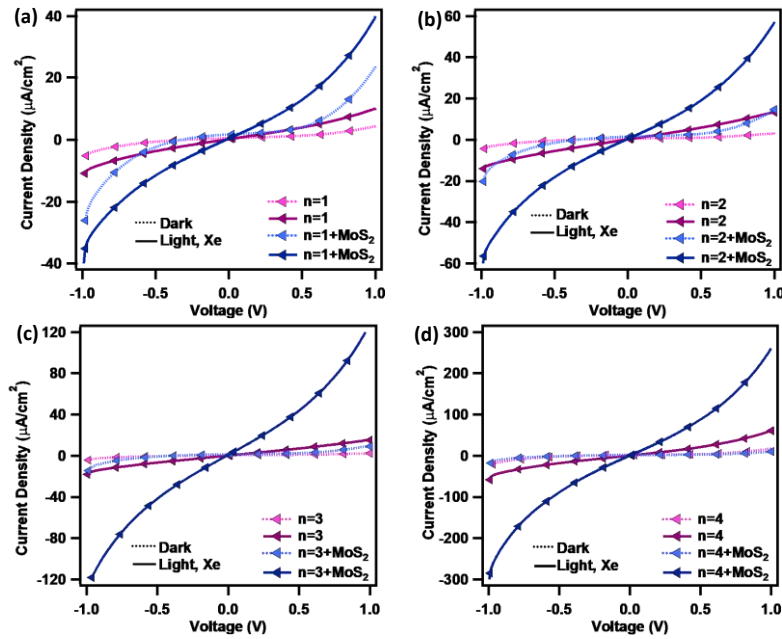


**Figure 3.12** (a-d) J-V curves measurement in light and dark under the excitation of Xenon lamp for  $(\text{BA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}$  ( $n=1-4$ ) and  $(\text{BA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1} + \text{MoS}_2$  (12.8 mM) hybrids ranging from -1 to +1.

### 3.7.3 Transient photocurrent for pristine RP perovskite $(\text{BA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}$ ( $n=2$ ) and its hybrid with $\text{MoS}_2$ with different concentrations

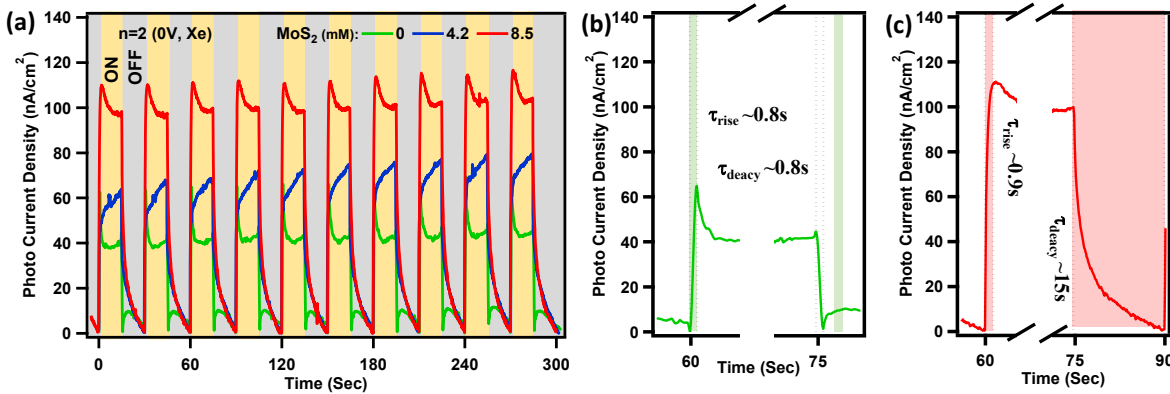


**Figure 3.13** (a) Transient photocurrent measurements under 1 Sun (Xe-lamp) illumination at zero bias condition for  $(\text{BA})_2(\text{MA})\text{PbI}_3$  and  $(\text{BA})_2(\text{MA})\text{PbI}_3 + \text{MoS}_2$  (4.2-8.5 mM) hybrids. (b-c) Rise ( $\tau_{\text{rise}}$ ) and decay ( $\tau_{\text{decay}}$ ) time for  $(\text{BA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}$  ( $n=2$ ) pristine and  $n=2 + \text{MoS}_2$  (8.5 mM) hybrid.

After that, I performed the transient photocurrent measurements with varying molar concentrations of  $\text{MoS}_2$  in order to verify the role that  $\text{MoS}_2$  plays in the transport characteristics of photogenerated charge carriers of RP perovskite ( $n=2$  and 4). The observation of these transient photocurrent responses can be performed utilizing potentiostat work station (**Section 2.12**). This work station is equipped with a manual shutter to turn on and off the illumination at every 15 seconds, therefore producing a pulsed excitation that is similar to a square wave. The pristine perovskite film ( $n=2$ ) exhibits a sharp increase in photocurrent (800 msec) to around 40  $\text{nA}/\text{cm}^2$  when it was illuminated with 1 Sun light at a bias of 0.0 V. However, when the light was switched off after 15 seconds, the photocurrent dropped rapidly at 800 msec (**Figure 3.13a-c**). Nevertheless, the incorporation of  $\text{MoS}_2$  at a concentration of 4.2 mM has led to an increase in photocurrent of around 63  $\text{nA}/\text{cm}^2$ . Over the 8.5 mM  $\text{MoS}_2$  doped perovskite film ( $n=2$ ), a comparable rapid increase in photocurrent (900 msec) to around 110  $\text{nA}/\text{cm}^2$  is observed. However, when the light is switched off, the photocurrent decays slowly over a period of 15 seconds (**Figure 3.13a-c**). It is possible to attribute the slow decay in the photocurrent of hybrids to the absence of HTM, which causes an imbalance between the extracted e-h pairs. This is because  $\text{MoS}_2$  extracts the electrons very efficiently, which

results in a large number of holes being left in the valence band of perovskite [Singh et al., 2019]. To have a better understanding for the dynamics of the photogenerated carrier, it is necessary to conduct investigations using appropriate HTM.

### 3.7.4 Transient photocurrent for pristine RP perovskite $(\text{BA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}$ ( $n=4$ ) and its hybrid with $\text{MoS}_2$ with different concentrations

As  $n=4$  perovskites have the lowest band gap (1.94 eV) among  $(\text{BA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}$ ,  $n=1-4$  RP perovskites, I have conducted an extensive study into  $\text{MoS}_2$  doped  $n=4$  perovskite films. The observation of a higher photocurrent density of around  $602 \text{ nA/cm}^2$  for a pristine  $n=4$  perovskite thin film (**Figure 3.14a**) under similar illumination conditions as discussed above. This higher photocurrent density indicates the generation of a significant number of electron hole pairs, which is a result of enhanced absorption in the visible region due to a lower energy band gap. Just like the  $n=2$  photodetector, the pristine  $n=4$  photodetector has shown a sharp rise in photocurrent (around 200 msec) and a rapid decay (around 200 msec) in transient photocurrent measurements (**Figure 3.14b-c**).

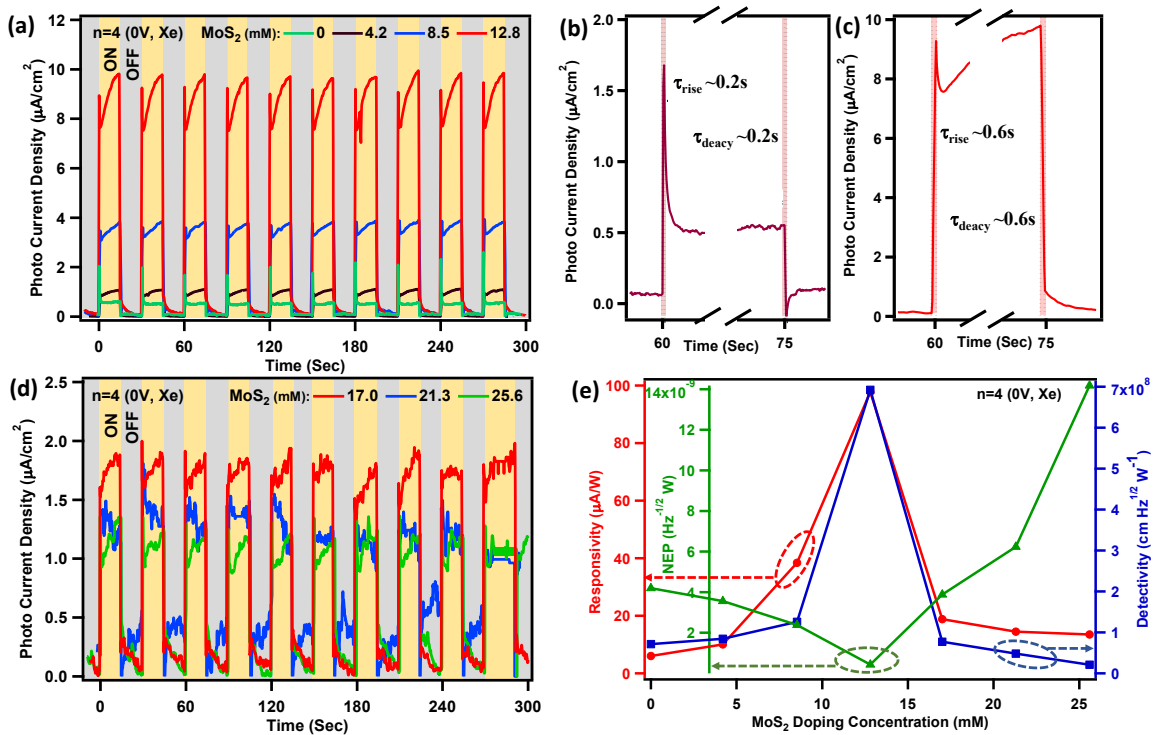


**Figure 3.14** (a) Transient photocurrent measurements under 1 Sun (Xe-lamp) illumination at zero bias condition for  $(\text{BA})_2(\text{MA})_3\text{PbI}_4$  and  $(\text{BA})_2(\text{MA})_3\text{PbI}_4 + \text{MoS}_2$  (4.2-12.8 mM) hybrids. Rise ( $\tau_{\text{rise}}$ ) and decay ( $\tau_{\text{decay}}$ ) time for (b-c)  $(\text{BA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}$  ( $n=4$ ) pristine and  $n=4 + \text{MoS}_2$  (12.5 mM) hybrid thin films. (d) Transient photocurrent measurements under 1 Sun (Xe-lamp) illumination at zero bias condition for  $(\text{BA})_2(\text{MA})_3\text{PbI}_4 + \text{MoS}_2$  (17.0-25.6 mM) hybrids. (e) Variation of responsivity (left axis-red color), NEP (left axis-green color) and detectivity (right axis) with MoS<sub>2</sub> doping concentration (mM) for  $(\text{BA})_2(\text{MA})_3\text{PbI}_4 + \text{MoS}_2$  hybrid based photodetector operated at 0.0 V bias under 1 Sun (Xe-lamp) illumination in ambient air conditions.

Moreover, the photocurrent response of the hybrids based on  $(\text{BA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}$  ( $n=4$ )+ $\text{MoS}_2$  increased to around  $1 \mu\text{A/cm}^2$  (4.2 mM  $\text{MoS}_2$ ), around  $3.8 \mu\text{A/cm}^2$  (8.5 mM  $\text{MoS}_2$ ), and around  $9.8 \mu\text{A/cm}^2$  (12.8 mM  $\text{MoS}_2$ ) (**Figure 3.14a**). This enhanced rise was seen in comparison to the reference device, which had a photocurrent response of around  $0.6 \mu\text{A/cm}^2$ . In addition to the enhanced photocurrent densities when compared to hybrids of  $(\text{BA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}$  ( $n=2$ )+ $\text{MoS}_2$ , it is noticed that hybrids of  $(\text{BA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}$  ( $n=4$ )+ $\text{MoS}_2$  exhibit considerably shorter photocurrent rise and decay durations (**Figure 3.14b-c**). In order to further verify the increased photocurrents for the perovskite- $\text{MoS}_2$  heterojunction, I conducted the photocurrent measurements on the pristine  $\text{MoS}_2$  drop-casted film-based photodetector. The results revealed that the photocurrent rise (around 6.2 seconds) and decay (around 15 seconds) timings were much slower (**Figure 3.15**). Moreover, the

photocurrent density for  $(\text{BA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}$  ( $n=4$ ) film is dramatically reduced when the doping concentration of  $\text{MoS}_2$  is increased further from 17 mM to 25.6 mM stepwise. However, these photodetectors have still shown a larger photocurrent when compared to the pristine  $(\text{BA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}$  ( $n=4$ ) film (**Figure 3.14d**). The reason for this decrease in the photodetector's response for heavily doped  $\text{MoS}_2$  in the RP perovskites film is that the presence of an excessive amount of  $\text{MoS}_2$  nanoflakes lowers the intensity of light that reaches the perovskite. This is because the excessive  $\text{MoS}_2$  flakes settle on the FTO substrate, which in turn reduces the amount of light that is transmitted through the perovskite. A consequence of the excessive presence of  $\text{MoS}_2$  is that it causes an increase in the number of junctions, which in turn causes to rise resistance of the films. Furthermore, optoelectronic parameters, which include photoresponsivity ( $R$ ), detectivity ( $D$ ), and noise equivalent power (NEP) are calculated to investigate their performance using the formula discussed in **Sub-Section 2.12.3** of **Chapter 2**.

### 3.7.4.1 J-V characteristics and Transient photocurrent for $\text{MoS}_2$ nanoflakes

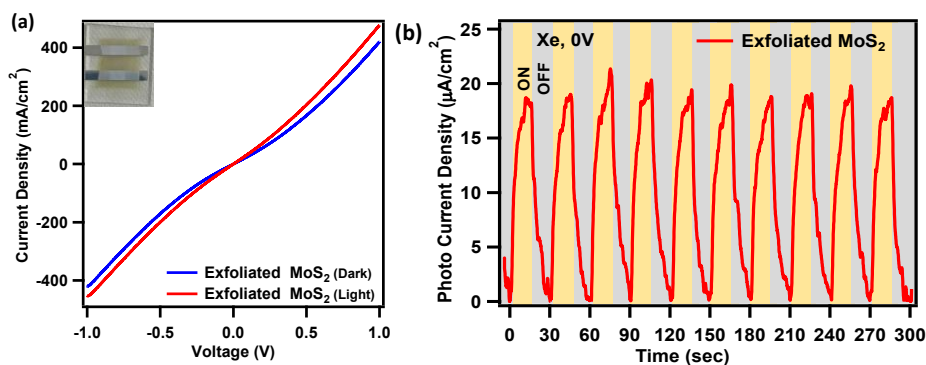


**Figure 3.15** (a) J-V curves measured under light (Xenon lamp) and dark conditions for  $\text{MoS}_2$  (12.8 mM). Inset shows digital camera image of actual device. (b) Transient photocurrent measurements (under the excitation of Xenon lamp) at zero bias condition for  $\text{MoS}_2$  (25.6 mM).

The transient photocurrent measurements that are shown in **figure 3.14a** and **figure 3.14d** are used to determine the difference between the  $J_{\text{light}}$  and  $J_{\text{dark}}$  values for pristine ( $n=2$  and 4) and  $\text{MoS}_2$  doped RP perovskite. With a pristine ( $n=2$ ) photodetector, the  $R$  is about  $0.4 \mu\text{A/W}$ . However, when the photodetector is doped with  $\text{MoS}_2$  at molar concentrations of 4.2 mM and 8.5 mM, the  $R$  increased to around  $0.63 \mu\text{A/W}$  and then around  $1.1 \mu\text{A/W}$  respectively. Similarly, to the pristine ( $n=2$ ) sample, the pristine RP perovskite ( $n=4$ ) sample has demonstrated of around  $6 \mu\text{A/W}$ . However, upon doping  $\text{MoS}_2$  with 4.2 mM, 8.53 mM, and 12.8 mM concentrations, the  $R$  is increased to around  $10 \mu\text{A/W}$ ,  $38.8 \mu\text{A/W}$ , and  $98 \mu\text{A/W}$ , respectively. In contrast, the  $R$  for excessive  $\text{MoS}_2$  doped RP perovskites reduced from around  $18.8 \mu\text{A/W}$  to around  $13.5 \mu\text{A/W}$  as the amount of  $\text{MoS}_2$  doping increased from 17 mM to 25.6 mM (**Figure 3.14e**). Despite this reduction, the  $R$  remains still higher than its RP perovskite counterpart ( $6 \mu\text{A/W}$ ). In this way, the 12.8 mM  $\text{MoS}_2$  doped RP perovskite hybrid has the ability to provide the best possible performance of a thin film photodetector. Moreover,  $D$  for the pristine photodetector ( $n=4$ ) is found to be only  $0.71 \times 10^8 \text{ cm Hz}^{1/2} \text{ W}^{-1}$ . Further, as the concentration of  $\text{MoS}_2$  increases from 4.2 mM to 8.5 mM in the hybrid photodetector, then there is a gradual rise in the  $D$  to  $1.26 \times 10^8 \text{ cm Hz}^{1/2} \text{ W}^{-1}$ . For 12.8 mM  $\text{MoS}_2$  concentration, there is a sharp rise in the  $D$  and reached to  $6.93 \times 10^8 \text{ cm Hz}^{1/2} \text{ W}^{-1}$  which is around 9.76 times higher than its pristine photodetector (**Table 3.2** and **Figure 3.14e**). Likewise, NEP is decreased about 9.76 times for 12.8 mM doped  $\text{MoS}_2$  hybrid photodetector. Furthermore,  $D$  is reduced, and NEP is increased, as anticipated from transient photocurrent measurements for the excessive doped hybrid photodetectors (17.00–25.6 mM). This is because of the low light-perovskite interaction and higher film resistance.

**Table 3.2** Responsivity ( $\mu\text{A/W}$ ), Detectivity ( $\text{cm Hz}^{1/2}/\text{W}$ ) and NEP ( $\text{W}/\text{Hz}^{1/2}$ ) vs different concentration of  $\text{MoS}_2$  for  $(\text{BA})_2(\text{MA})_3\text{PbI}_{13} + \text{MoS}_2$  hybrid based photodetector operated at 0.0 V bias under 1 Sun (Xe-lamp) illumination in ambient air conditions.

| MoS <sub>2</sub> Doping Concentration (mM) | Responsivity (μA/W) | Detectivity [cm Hz <sup>1/2</sup> W <sup>-1</sup> ] | NEP [Hz <sup>-1/2</sup> W] |
|--------------------------------------------|---------------------|-----------------------------------------------------|----------------------------|
| 0                                          | 0.60                | 0.71×10 <sup>8</sup>                                | 4.2×10 <sup>-9</sup>       |
| 4.2                                        | 1.00                | 0.84 ×10 <sup>8</sup>                               | 3.56×10 <sup>-9</sup>      |
| 8.5                                        | 3.84                | 1.26×10 <sup>8</sup>                                | 2.39×10 <sup>-9</sup>      |
| 12.8                                       | 9.77                | 6.93×10 <sup>8</sup>                                | 0.43×10 <sup>-9</sup>      |
| 17                                         | 1.88                | 0.77×10 <sup>8</sup>                                | 3.88×10 <sup>-9</sup>      |
| 21.3                                       | 1.45                | 0.48×10 <sup>8</sup>                                | 6.24×10 <sup>-9</sup>      |
| 25.6                                       | 1.35                | 0.21×10 <sup>8</sup>                                | 14.2×10 <sup>-9</sup>      |

### 3.7.5 Stability analysis for RP perovskite and RP perovskite-MoS<sub>2</sub> hybrid

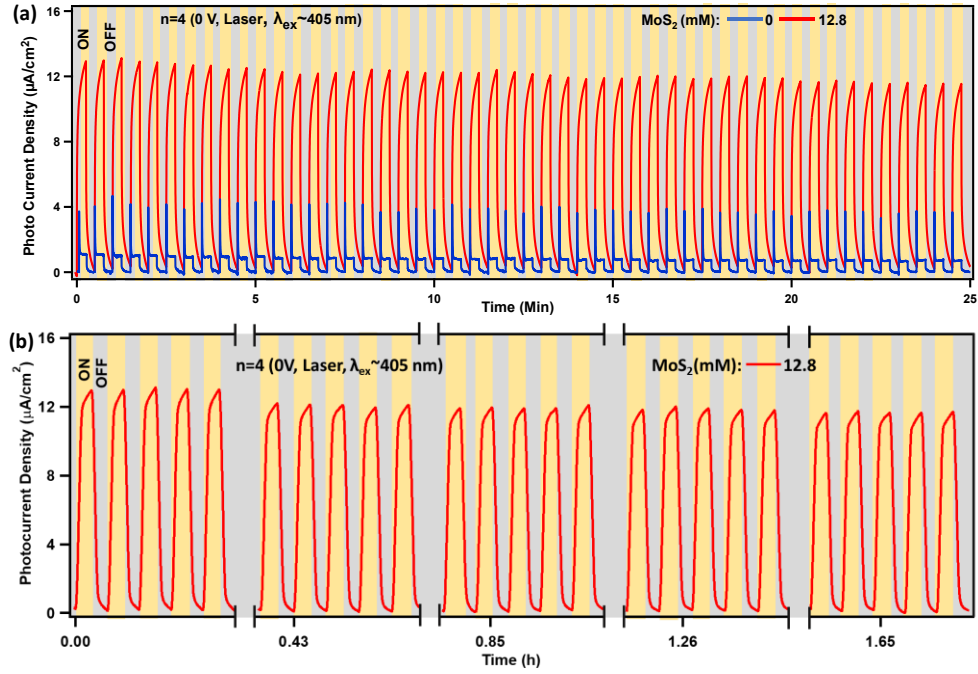


**Figure 3.16** Transient photocurrent measurements performed under DPSS laser ( $\lambda_{\text{ex}} \sim 405 \text{ nm}$ ,  $\sim 630 \text{ mW/cm}^2$ ) illumination at zero bias condition for un-encapsulated  $(\text{BA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13}$  and  $(\text{BA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13} + \text{MoS}_2$  (12.8 mM) hybrid based photodetectors measured in ambient air condition for (a) 50 cycles and (b) 200 cycles.

Finally, long cycling transient photocurrent measurements are performed in ambient air conditions (15 seconds ON and 15 seconds OFF) at 0 V bias under a DPSS laser ( $\lambda_{\text{ex}} \sim 405 \text{ nm}$ , around  $630 \text{ mW/cm}^2$ ) without encapsulation of devices in order to analyze the stable performance of hybrid material as compared to pristine sample. For the hybrid photodetector with 12.8 mM concentration of MoS<sub>2</sub>, the performance has been relatively stable, with a slight reduction of around 7% in the photocurrent density after 50<sup>th</sup> cycles ( $t=0 \text{ min}$ , around  $12.89 \text{ } \mu\text{A/cm}^2$  and  $t=25 \text{ min}$ , around  $11.97 \text{ } \mu\text{A/cm}^2$ ). On the other hand, the pristine RP perovskite-based detector has demonstrated a noticeable reduction of around 39% ( $t=0 \text{ min}$ ,  $1.1 \text{ } \mu\text{A/cm}^2$  and  $t=25 \text{ min}$ ,  $0.67 \text{ } \mu\text{A/cm}^2$ ) under similar conditions (**Figure 3.16a**). Furthermore, 200-cycles transient photocurrent measurements are carried out for the freshly prepared hybrid photodetector under similar conditions as discussed above. In this case the peak photocurrent response is fairly stable with slight reduction of  $\sim 9.6\%$  in the peak photocurrent density ( $t=0.0 \text{ h}$ ,  $12.95 \text{ } \mu\text{A/cm}^2$  and  $t=1.67 \text{ h}$ ,  $11.70 \text{ } \mu\text{A/cm}^2$ ) (**Figure 3.16b**). It is also interesting to see that the peak photocurrent response profile after 200 cycles is still identical to the first cycle trend. During the experiment, it is concluded that the incorporation of MoS<sub>2</sub> not only resulted in an increase in the photo current response, but it also made the RP perovskites more stable for the application in ambient air environment.

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