



Atmospheric synthesis of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite films for enhanced photocatalytic degradation of methylene blue under solar light: Impact of annealing treatment

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Received: 18 February 2025

Accepted: 15 August 2025

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ABSTRACT

In this work, Perovskite $\text{CH}_3\text{NH}_3\text{PbBr}_3$ thin films were grown on glass substrates by mixing PbBr_2 with $\text{CH}_3\text{NH}_3\text{Br}$ in DMF using dip coating technique in air atmosphere at 30 s of dip time. In order to investigate the formation of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite phase, the films were subjected to air annealing treatment for one hour at 100 °C. The deposited films were characterized by XRD, SEM, Raman, and FTIR. The bandgap was calculated by Tauc plot equation using MATLAB Software. The results revealed the presence of cubic ($\text{CH}_3\text{NH}_3\text{PbBr}_3$) phase and the formation of organic-inorganic halide bond in the inorganic framework and organic CH_3 stretching/bending of C–H bond in the films. The surface film morphology changed from a porous surface to a homogeneous structure with large grain sizes after annealing at 100 °C. The UV–visible analysis of the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ films shows transparency in the visible range after annealing treatment, with a slight decrease in the optical gap from 2.45 to 2.14 eV. After air annealing, the photocurrent of the films significantly increases from 2 to 11 mA, while the photosensitivity decreased from 4.7 V down to 1.58 V. In terms of methylene blue (MB) degradation, the annealed perovskite film had a better degradation ratio of 78.25% under solar sunlight for 3 h. This will open new ideas for the development of perovskite films to solve the photocatalytic problems and treat organic polluted water under solar sunlight.

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1 Introduction

Given the importance of protecting the environment from pollution caused by harmful constituents (gases, chemicals, waste, etc.) that can affect air, water, and soil. Faced with the limitations of conventional treatment methods, new solutions have been developed, such as photocatalysis under visible light that take major challenges of the researchers to developing more effective degradable materials. [1] When the reagent is exposed to high-energy light, electron-hole pairs (e^-/h^+) are generated and react with water and oxygen to form reactive oxygen species (ROS), hydroxyl radicals ($\cdot\text{OH}$) and superoxide anions ($\cdot\text{O}_2^-$, $\text{O}_2^{\cdot-}$), with oxidation potentials high enough to non-selectively decompose organic and inorganic pollutants into harmless end products such as carbon dioxide, water, and mineral acids [2]. However, recent research has focused on developing new compounds that are more photocatalytic under visible light. Various materials are used as photocatalysts to effectively decompose pollutants, such as titanium dioxide (TiO_2), zinc oxide (ZnO), tungsten oxide (WO_3), and cadmium sulfide (CdS) [3] Halogenated perovskites also have high photocatalytic capacity under UV or visible light, thanks to their powerful free radicals that degrade organic compounds. The integration of these materials into hybrid systems represents a promising avenue for increasing the efficiency and sustainability of remediation technologies [4]. This comprehensive review discusses how halide perovskites (e.g., ABX_3 , where $X = \text{Cl}^-$, Br^- , I^-) absorb UV/visible light, generate (e^-/h^+) pairs, and subsequently form reactive free radicals that efficiently degrade organic dyes and pollutants [5]. Among them, perovskite $\text{CH}_3\text{NH}_3\text{PbBr}_3$ is organic-inorganic hybrid material with unique structural properties and promising applications in optoelectronics, photocatalysis, and photovoltaics, which is a key material for solar energy conversion. Along with significant efforts in the fields of solar cells and photovoltaics, perovskites are being studied as light absorbers in photodetectors. This is due to their cubic ABX_3 crystal structure: $A = \text{CH}_3\text{NH}_3^+$ (methylammonium, organometallic), $B = \text{Pb}^{2+}$ (lead, metal, cation), and $X = \text{Br}^-$ (halide, anion), and their excellent crystallinity. Furthermore, $\text{CH}_3\text{NH}_3\text{PbBr}_3$ combines the advantages of both organic and inorganic materials with good mechanical flexibility and high electron mobility. This dual property makes it a promising candidate for diverse optoelectronic applications. [6].

Compared with the extensive efforts in solar cells and photovoltaic fields, the study of perovskites as light absorbers in photodetectors is relatively less extensive, and previous reports have focused more on organic-inorganic hybrid perovskites [7]. To grow $\text{CH}_3\text{NH}_3\text{PbBr}_3$ thin films, various vacuum elaboration techniques have been employed, such as the Anti-Solvent Method, Vapor-Assisted Solution Method, solid-state reaction, and co-precipitation methods. (Poglitsch et al. 1987) [8] found that the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ thin films formed by evaporation exhibit an ordered structure, which is essential for charge movement due to their large bandgap of 2.2 eV and efficient p-type conductivity. (Harisingh et al. 2018) [9] demonstrated the photochemical activity of CsPbBr_3 and $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite thin films under 532 nm pulsed laser irradiation in ultra-high vacuum, promoting the photo-dissociation of adsorbed ethyl chloride (EC). Temperature-programmed desorption (TPD) analysis showed significantly higher photoreactivity efficiency compared to UV-excited EC molecules on metallic and oxide surfaces. (Sheng et al. 2015) [10] found that the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ cell was fabricated using the vapor-assisted method, which involved several steps, including the spin coating of a PbBr_2 solution. $\text{FA}_{1-x}\text{MA}_x\text{PbI}_3$ (FA = formamidinium and MA = methylammonium) perovskite films, in a recent study, (Elisabeth et al. 2023) [11]. demonstrated the high thermal stability of FAPbI_3 films compared to MAPbI_3 . Analysis using micro-photoluminescence (TRPL) showed an extended cumulative life of the importers, indicating improved film quality. Understanding the degradation of methylene diammonium and its role in phase-stabilizing formamidinium lead triiodide is essential. Some studies also demonstrate the tremendous potential of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ (MAPbBr_3) perovskite thin films in photocatalysis via various approaches. For example, (Wu et al 2018) [12] showed that in a mixed-halide architecture, $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ powders prepared by employing a facile light-assisted halide-exchange method in aqueous halide solution at room temperature exhibit bandgap suppression that enhances charge carrier separation, allowing hydrogen evolution at $651 \mu\text{mol/h}^1$ under visible light ($\lambda \geq 420 \text{ nm}$), with a solar chemical efficiency of 1.05%. In a related study, hybridization of MAPbBr_3 nanocrystal films with $\text{Pt/Ta}_2\text{O}_5$ resulted in an increased rate of H_2 production [13]. Furthermore, MAPbBr_3 thin film deposited under green laser irradiation (532 nm) showed better photo-dissociation of ethyl chloride compared

to conventional metal or oxide surfaces [14]. However, all of these methods are slightly more expensive due to their use in vacuum environments, making it difficult to control film compositions. Therefore, dip coating was the first technique used to prepare $\text{CH}_3\text{NH}_3\text{PbBr}_3$ in atmospheric conditions due to its simplicity, cost-effectiveness, and ability to produce high-quality films. This method enables uniform coating over large areas, which is essential for optoelectronic device applications. The process can use low-cost raw materials, reducing overall material costs. This technique ensures uniform film thickness, which is critical for stable optical and electronic properties [15]. It features strong absorption in the visible spectrum. A well-defined bandgap, typically (depending on the composition), is present. Sufficient charge carrier mobility is required for photovoltaic applications. High purity and crystallinity of the deposited films have been reported, resulting in improved device performance. This method can be easily scaled up, facilitating the mass production of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ films. On the other hand, heat treatment has an important role in improving the structural, optical, and electronic properties of perovskite thin films based on organometallic halide materials such as $\text{MAPb}(\text{I}_3, \text{Br}_3)$ films. This process increases the grain size and uniformizes the morphology of the films, which reduces grain boundary density and improves charge carrier mobility, resulting in better photocatalytic performance [16, 17].

In this work, the dip coating process was first used to prepare successfully perovskite $\text{CH}_3\text{NH}_3\text{PbBr}_3$ films in air atmosphere. This method permits the deposition of a uniform film over large areas, which is essential for optoelectronic device fields. The influence of annealing treatment at 100 °C on the structural, morphological, optical, and photodetection behavior was investigated. $\text{CH}_3\text{NH}_3\text{PbBr}_3$ films have also demonstrated promising photocatalytic capabilities for different cycles under sunlight, particularly in the degradation of methylene blue (MB) by adding titanium dioxide.

2 Experimental parts

2.1 Powder preparation

The mixture of $\text{CH}_3\text{NH}_3\text{Br}$ (MABr) was described as follows: 30 mL of methylamine (SEGMA-ALDRICH 40wt. % in H_2O) 32.3 mL of hydroiodic acid (57 wt. %

in H_2O , SEGMA-ALDRICH) and methanol (TCl) were placed in a 250 mL bottom flask at room temperature with continuous stirring for 2 h, and the solvents were gently removed at 50 °C. The beaker was covered with aluminum foil and left overnight (~8 h) without any disturbance. The resulting suspension was washed with an ethanol and water mixture and then filtered. The washing process was carried out three times. After filtration, the solid was collected and dried for 24 h at 60 °C in a vacuum oven.

2.2 Films preparation

The obtained $\text{CH}_3\text{NH}_3\text{Br}$ (MABr) powder with white finer particles was used to deposit the films using a dip coating technique. The $\text{CH}_3\text{NH}_3\text{PbBr}_3$ precursor solutions were prepared by dissolving MABr and PbBr_2 (SIGMA-ALDRICH $\geq 98\%$) in N-dimethylformamide (DMF) solvent: 0.8 mmol of PbBr_2 dissolved in 10 mL of (DMF), and 0.9 mmol of MABr dissolved in 10 mL of (DMF). The obtained solution was mixed for 2 h; it became transparent and homogeneous.

Before the deposition, the glass substrates ($2 \times 2 \text{ cm}^2$) were cleaned by both acetone and ethanol ultrasonic baths for 5 min, and then dried in air. Then, the MAPbBr_3 films were deposited using the dip coating technique by immersing the glass substrates one time during 1 min in air atmosphere. The dip coating technique offers a simple, scalable, and cost-effective route for achieving uniform and continuous perovskite films over large areas, with controllable thickness. Additionally, dip-coated films can exhibit improved crystal quality and better grain connectivity, which can lead to enhanced photophysical and photocatalytic performance [18].

2.3 Heat treatment

To achieve the pure $\text{CH}_3\text{NH}_3\text{PbBr}_3$, the coated glasses were annealed at 100 °C, in a programmable muffle furnace (PROTHERM) at air atmosphere. The thermal cycle started with a ramp of 10 °C/min, followed by maintaining the desired temperature at that fixed temperature of 100 °C for 1 h. Finally, the heated films were allowed to cool in air at a cooling rate of -10 °C/min based on thermocouple measurements. In fact, below 100 °C MAPbBr_3 film is amorphous with high impurities. The heat treatment at this temperature leads to the stabilization of organic compounds with good crystallinity. Furthermore, above this temperature

(100 °C), organic compounds, such as CH_3NH_3^+ were decomposed and Br⁻halides were evaporated [19]. Figure 1 summarizes the procedure for preparing $\text{CH}_3\text{NH}_3\text{PbBr}_3$ thin films by dip coating.

3 Materials and methods

The morphology of the films was determined using a field emission scanning electron microscope (FE-SEM Hitachi SU 8030) operated at 40 V and 40 mA, which is equipped with an EDX spectrometer to determine the chemical composition of the films. The phase structure and crystal size of the films were studied by X-ray diffraction (XRD D8 advanced using Cu-K α radiation ($\lambda = 0.154056$ nm) in $\theta/2\theta$ mode with a 0.02° step. The

average crystallite size was determined by the Scherer method as the following equation [20]:

$$D = \frac{0.9}{\beta \cos \theta - 4\varepsilon \cdot \sin \theta} \quad (1)$$

where 0.9 is a dimensionless shape factor, β is the X-ray wavelength (in rad) the line broadening at half the maximum intensity (FWHM full width half maximum), θ is Bragg's angle (in rad) and ε is the average internal micro-strain ($\varepsilon = a - a_0/a_0$), a_0 is the lattice parameter of the bulk phase ($a_0 = 5.92$ Å, 00–001–0647). The lattice parameter was calculated from XRD patterns using Bragg's law:

$$2 \cdot d_{(hkl)} \times \sin \theta = n\lambda \quad (2)$$

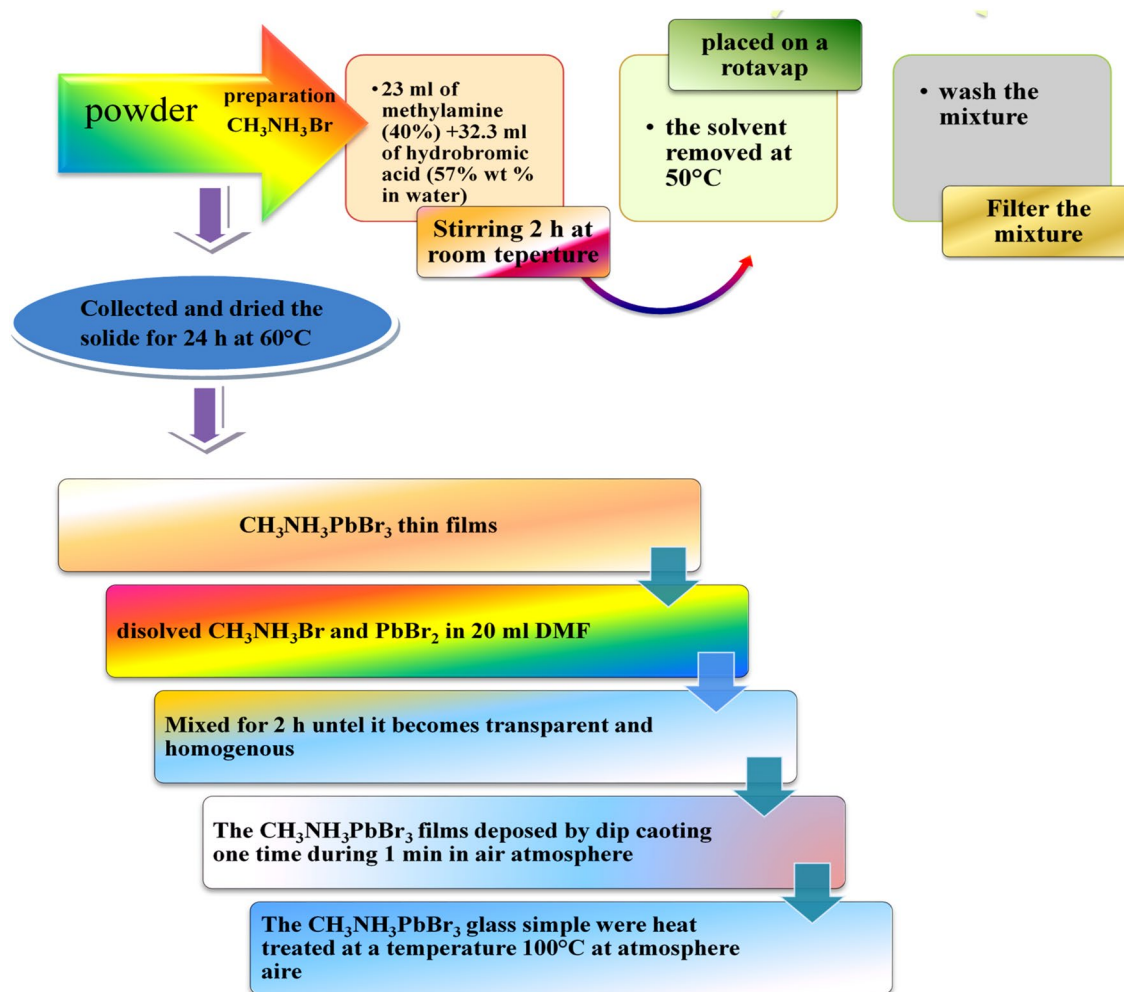


Fig. 1 The chart for the procedure for preparing $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite thin films by dip coating

Where d_{hkl} is the interreticular distance existing between the atomic layers, in our case $n = 1$ (in the first order of reflection), λ is the X-ray wavelength ($\lambda = 0.154056$ nm).

Fourier transform infrared (FTIR) spectroscopy was performed using a Perkin-Elmer Spectrum One spectrometer with a spectral resolution of 4 cm^{-1} , covering a range of $(500\text{--}4000)\text{ cm}^{-1}$. Perovskite powders obtained by scraping the films were mixed with potassium bromide KBr granules for measurements.

Raman spectroscopy was performed using a Bruker Centrera spectrometer equipped with a 664 nm diode laser operating at an effective power of 30 mW. The measurements were performed in a backscattering environment at room temperature to obtain complementary information on the vibrational and structural properties of the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ films.

The film transmittance synthesized on the glass substrates was measured by using a Perkin-Elmer UV-VIS Lambda 19 spectrophotometer in the $(190\text{--}1000)$ nm spectral range. The weather baseline correction was applied in UV-Vis measurements using Origin software.

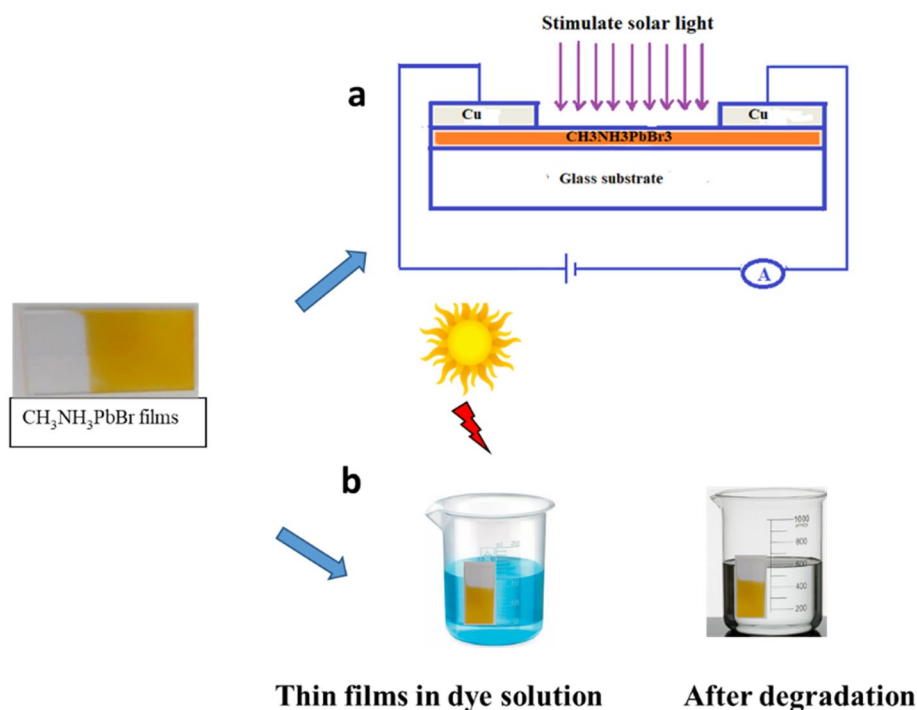
The photocurrent – voltage (I-V) characteristics of solar cells were determined under solar simulated light (CPS Sun test System, Germany) (AM1.5G , 100 mW/cm^2) illumination with a solar simulator or with an emission between 320 and 800 nm. The coated

glass ($1 \times 1\text{ cm}^2$) samples were vertically exposed to the solar simulated light source at a distance of 5 cm. This method involves real-time measurement using a two-point probe. The input voltage for the two-point measurement was fixed at 5 V when this light irradiation was vertically projected onto the sample surface in a dark test chamber, where the photocurrent signal is then detected using the precision source measurement unit. The current intensity was measured from 0 to 5 V in a dark room and then using solar simulated light. The samples were projected for 30 s in the dark and light illumination at ambient temperature during the optodetection test.

Photocatalysis of as-deposited and annealed $\text{CH}_3\text{NH}_3\text{PbBr}_3$ thin films was realized under sunlight, using a concentration of $2 \times 10^{-5}\text{ mol.L}^{-1}$ and a volume of 5 ml of (MB) solution.

The BM solution was exposed to solar light radiation for 30 min while being stirred in the dark to achieve equilibrium adsorption-desorption of the catalyst surface. The absorbance of the BM solution was measured every 30 min for 3 h by UV-visible absorption photometer at 664 nm (The absorption values 664 were obtained from UV-Vis spectroscopic measurements, representing the absorption at the maximum wavelength of methylene blue, approximately 664 nm) (Fig. 2a). The degradation rate of 2.5

Fig. 2 Schematic illustration of: **a** Optodetection test of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite film under stimulated solar light, **b** photodegradation of (MB) solution under solar light



$\times 10^{-5}$ mol of MB solutions was calculated according to the following formula [7]:

$$D(\%) = \frac{C_0 - C}{C_0} \cdot 100 \quad (3)$$

The reaction rate of as-deposited and annealed $\text{CH}_3\text{NH}_3\text{PbBr}_3$ thin films has been calculated according to the following formula [21]:

$$-\ln\left(\frac{C_0}{C_t}\right) = K_{app} \cdot t \quad (4)$$

here: C_0 is initial concentration at $t = 0$ (before irradiation) and C_t is the concentration after deferent irradiation at time.

The schematic illustration of opto-detection test of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ film under stimulated sunlight and photodegradation of (MB) solution under solar light are presented in (Fig. 2).

4 Results and discussion

4.1 Structure and morphology

To study the phases of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ films before and after annealing treatment at 100°C , the XRD pattern was obtained (Fig. 3). The identification and assignments of the acquired XRD patterns were determined using the JCPDS data for cubic- $\text{CH}_3\text{NH}_3\text{PbBr}_3$ (00–001–0647). Before annealing, the XRD pattern showed small diffraction peaks at 15.2° , 21.4° , 30.4° , 33.9° , 43.4° , and 46.0° , corresponding to the (100), (110), (200), (210), (220) and (300) planes of the cubic $\text{CH}_3\text{NH}_3\text{PbBr}_3$ structure, respectively, indicating a low crystallinity of the deposited film [22]. After annealing, the appearance of minor (111), (211) and (400) peaks, with a clear increase in the intensity of (100) and (200) peaks and a shift of peak positions to higher angles after annealing treatment, was shown (Fig. 3). This suggests that annealing treatment changes the atomic arrangement and improves the film growth, resulting in good quality film crystallinity, as obtained by (Yuan et al. 2019) [21].

Table 1 presents the variation of the lattice parameter (a), crystallite size (D), dislocation density (δ),

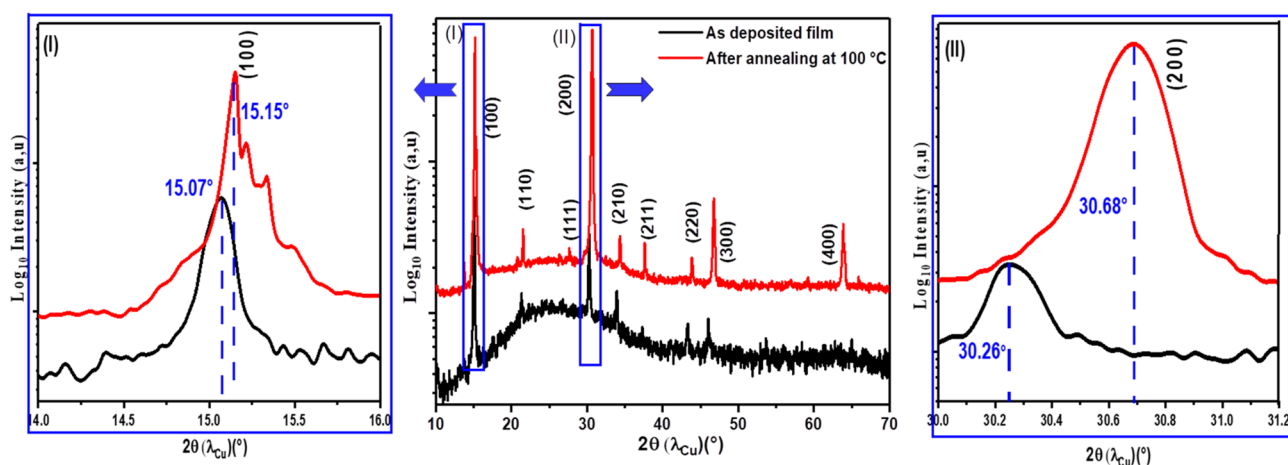


Fig. 3 XRD Spectra of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite films before and after annealing at 100°C

Table 1 Structural parameters of the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite films before and after annealing at 100°C

Heat temperature	(hkl)	Peak position ($^\circ$)	a ($\text{\AA}$)	ε (10^{-3})	D (nm)	FWHM (rad)	δ ($\times 10^{-4} \text{ nm}^{-2}$)
As deposited film	(100)	15.07	0.588	4.486	48.99	0.160	2.873
	(200)	30.26	0.584	2.630	40.46	0.163	3.927
100°C	(100)	15.15	0.591	2.198	59.57	0.157	0.699
	(200)	30.68	0.589	2.799	46.79	0.166	4.567

and micro-strain (ϵ) of a cubic-($\text{CH}_3\text{NH}_3\text{PbBr}_3$) phase for (100) and (200) peaks before and after annealing at 100 °C. The shift in the (100) and (200) diffraction peaks location led to an increase in the lattice parameter and the micro-strain in the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ crystal, as seen in Table 1. The average crystalline sizes of the as-deposited film were found to be 48.99 and 40.46 nm, respectively [23]. The widening of XRD diffraction peaks may result from the enlargement of the crystallite size (59.57, 46.79 nm), suggesting a coalesced surface morphology that could be found after annealing treatment, as seen in Table 1. The increase in the crystallite size after annealing temperature resulted in a decrease in dislocation density, a decrease in the defects, recrystallization, and coalescence of crystallites [24, 25]. Similar observations were obtained for spin-coating perovskite thin films deposited at 100 °C in previous works [11, 26].

Figure 4 shows SEM images of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ films before and after annealing at 100 °C in air for 1 h. EDX analysis was conducted and the results are presented in Fig. 4, confirming the intended elemental composition. After annealing treatment, the film contains lead (Pb), ranging from (23.8 ± 0.07) at. % to (24.2 ± 0.07) at.

%, and bromine (Br), ranging from (53.2 ± 1.59) at. % to (53.5 ± 1.59) at. %. Lead is well known for its toxicity to humans and the environment. The nitrogen content, between (16.7 ± 0.08) at. % and (17.8 ± 0.08) at. %, is not typically associated with toxicity in most compound forms [27].

Therefore, the annealing treatment of the film presents a deficiency to the oxygen, which results in a high affinity between N and H atoms as compared with that between N and O atoms. (Zheng et al. 2016) [28] found similar results for $\text{CH}_3\text{NH}_3\text{PbBr}_3$ films annealed at 100 °C through in situ large area control. Before annealing, $\text{CH}_3\text{NH}_3\text{PbBr}_3$ film has a porous surface whose cracks appeared around the holes with irregularly shaped nodules (Fig. 4a). This result can be explained by the high formation enthalpy of the dip-coated film, which allows low mobility and difficulty of diffusion of atoms on the surface film during deposition. This suggests that the surface energy is maximum for a film whose thermodynamic state is unstable according to the (200) preferential orientation [29]. Thermal annealing leads to an increase in the size of the grains, spherical shape with more grain boundaries. The spherical and large grain shape is a

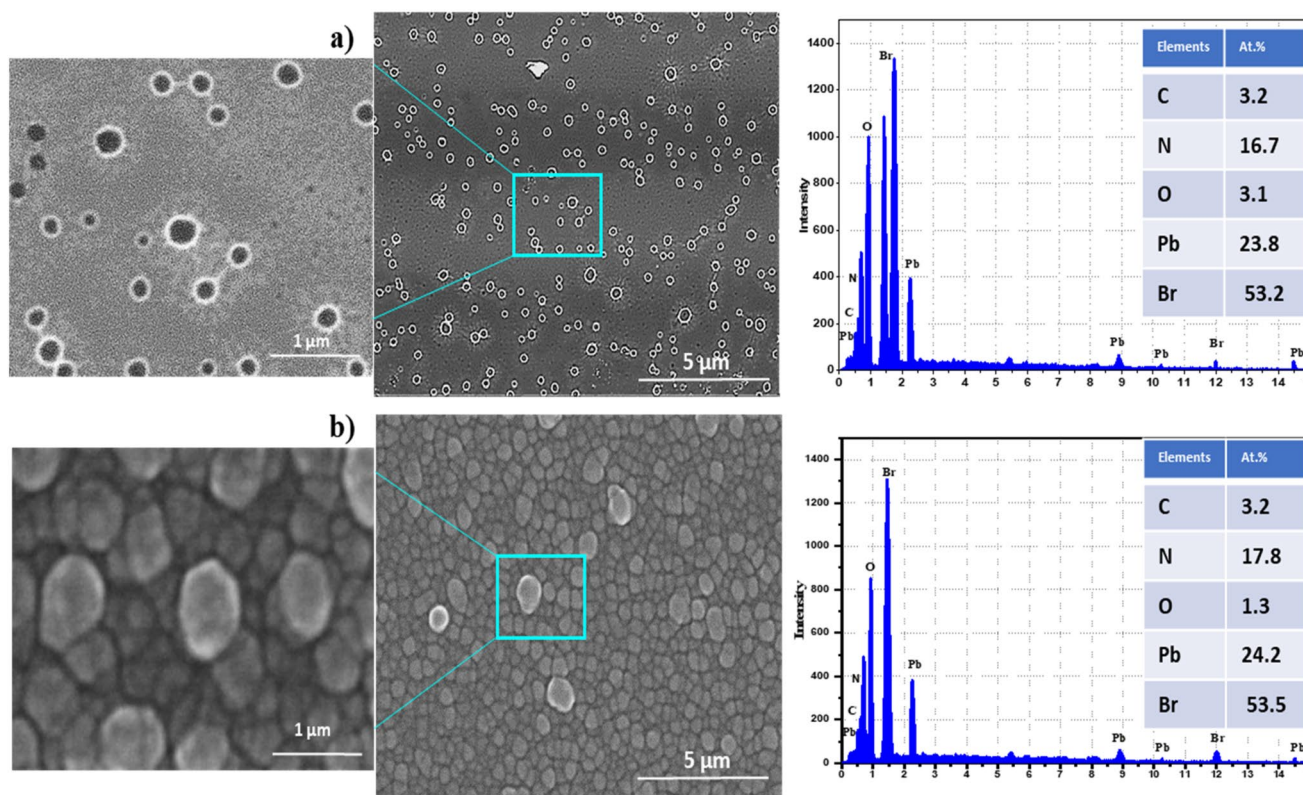


Fig. 4 SEM surface morphology of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite films: **a** before, and **b** after annealing at 100 °C

direct result of the domination of surface energy after thermal annealing and the system appears in a thermodynamic state close to the equilibrium state [30].

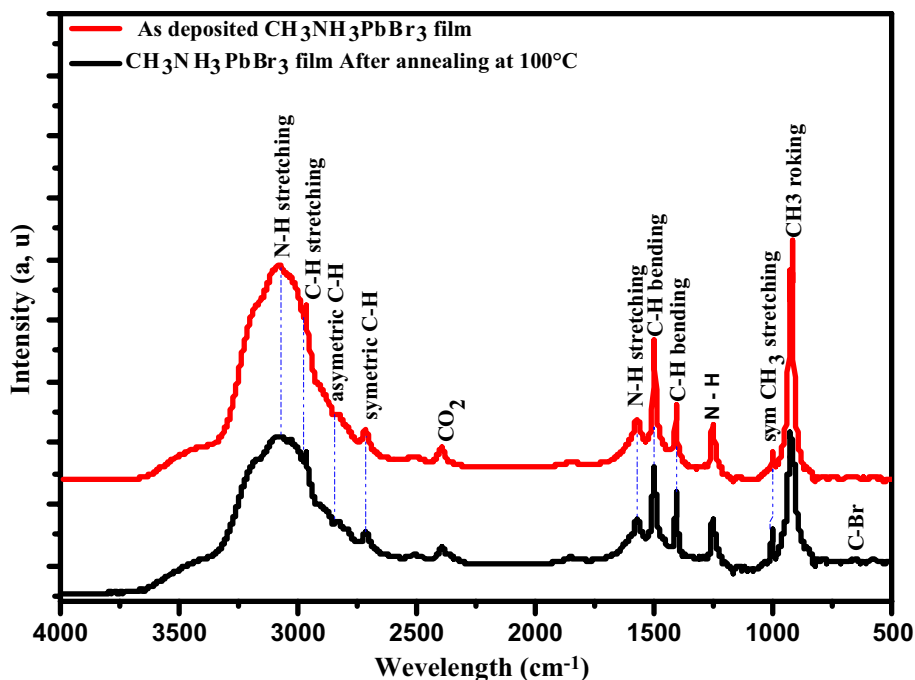
Thus, annealing treatment significantly affects the crystallinity and atomic arrangement of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ thin films by providing thermal energy that thermodynamically enables the atoms in the stable lattice structure and increases carrier mobility that reduces defects density, decreasing grain boundaries; improving adhesion and uniformity of the film [31].

Figure 5 illustrates the FTIR spectra of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ thin perovskite films before (black line) and after annealing at 100 °C (red line), covering the spectral range of (500–4000) cm^{-1} . The spectra highlight key vibrational modes corresponding to C–H, N–H, and C–Br stretching, which are strongly affected by the annealing process. At the higher wave number region (3230–3550 cm^{-1}), strong and broad absorption peaks are observed corresponding to N–H stretching vibrations. These bands, which are characteristic of primary amine groups, slightly shifted after the annealing treatment, reflecting changes in the hydrogen-bonding environment. Thus, the annealing process reduces the hydrogen-bonding strength, as indicated by the narrower and less intense N–H bands in the annealed film. This is attributed to reduced moisture content or structural reorganization within the perovskite $\text{CH}_3\text{NH}_3\text{PbBr}_3$ lattice [32]. In the CH

stretching region (2800–3000) cm^{-1} , two distinct peaks at 2856 and 2927 cm^{-1} were detected, corresponding to symmetric and asymmetric C–H stretching of methyl groups [33]. The region near 2400 cm^{-1} may correspond to the asymmetric stretching vibration of atmospheric CO_2 [34].

After annealing, these peaks show an increase in the intensity, indicating an enhanced vibrational response, likely due to improved structural ordering and reduced lattice defects. This observation aligns with the thermal stabilization of the organic–inorganic framework. The mid-wavenumber region (1400–1600) cm^{-1} reveals prominent peaks at 1465 and 1501 cm^{-1} , attributed to C–H bending vibrations, and 1576 cm^{-1} , corresponding to N–H stretching. After annealing treatment, these peaks become sharper and more defined, suggesting enhanced crystallinity and reduced disorder within the organic cation framework. At lower wavenumbers (680–485) cm^{-1} , bands associated with C–Br stretching vibrations were observed. These bands are clearly pronounced after annealing, indicating enhanced interaction between PbBr_6 octahedra and the organic cation. The increased intensity and clarity of these peaks after annealing confirm the grain coalescence of the perovskite $\text{CH}_3\text{NH}_3\text{PbBr}_3$ film. Additionally, the peak obtained at 921 cm^{-1} , attributed to CH_3 rocking vibrations, becomes strong after annealing, indicating the

Fig. 5 FTIR measurement spectra of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite films before and after annealing at 100 °C



improved alignment of the methylammonium cation within the perovskite $\text{CH}_3\text{NH}_3\text{PbBr}_3$ lattice. Overall, the FTIR spectral changes are due to a reduction of moisture sensitivity, enhancement of the vibrational stability, and good crystallinity of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ thin films. These emphasize the important role of air annealing at a temperature not exceeding 100°C , which is optimized for the photodetector device [35, 36]. Similar results were obtained by (Xie et al. 2016.,) [37] for $\text{CH}_3\text{NH}_3\text{PbBr}_3$ thin films deposited by dip coating process and annealed at 100°C .

Figure 6 shows the Raman spectra of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ thin perovskite films before annealing and after annealing in $(50\text{--}2000)\text{ cm}^{-1}$ region. In the intermediate wavenumber region, sharp and intense bands at 970 and 1480 cm^{-1} were detected, corresponding to the C–N stretching and NH_3^+ asymmetric bending, respectively. Moreover, the clearly defined rocking mode at 1249 cm^{-1} and the twisting mode at 1593 cm^{-1} of NH_3^+ bending in MAPbBr_3 perovskite were observed, indicating a high sensitivity of the MA^+ cation vibrational modes to the environment. The rocking mode at 924 cm^{-1} , with the opposite frequency variation trends, slightly appeared.

The sharp and intense bands at 1001 , 1370 , 1403 , 1544 , and 1614 cm^{-1} are from the C–N stretching, CH_3 symmetric deformation, CH_3 asymmetric deformation,

NH_3 asymmetric deformation, and NH_3 twisting, respectively [38], were also detected. These observations showed structural and vibrational changes induced by the annealing process [39]. In the low Raman wavenumber region, three weak peaks are observed at 59 , 95 , and 125 cm^{-1} , corresponding to lattice vibrational modes of the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite phases the peak observed at 59 cm^{-1} is indeed attributed to the Pb–Br stretching vibrations within the PbBr_6 octahedral framework. This relationship highlights the interactions within the inorganic sublattice of lead bromide perovskites. The peak at 95 cm^{-1} is associated with the rocking or bending mode of the methylammonium (MA^+) cation, representing its dynamic coupling with the inorganic lattice. Thus, the peak at 125 cm^{-1} is related to the torsional mode of the MA^+ cation, which involves a rotational motion and a coupling between the organic cation and the inorganic part. These low wavenumber modes are critical for understanding the structural dynamics and interactions within the hybrid perovskite material, as they reflect the degree of coupling between the organic and inorganic components that govern its stability and optoelectronic properties [40, 41].

Table 2 summarizes the vibrational modes of the hybrid perovskite $\text{CH}_3\text{NH}_3\text{PbBr}_3$ compound, detailing their molecular symmetry, character, and

Fig. 6 Raman measurement spectra of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite films before and after annealing at 100°C

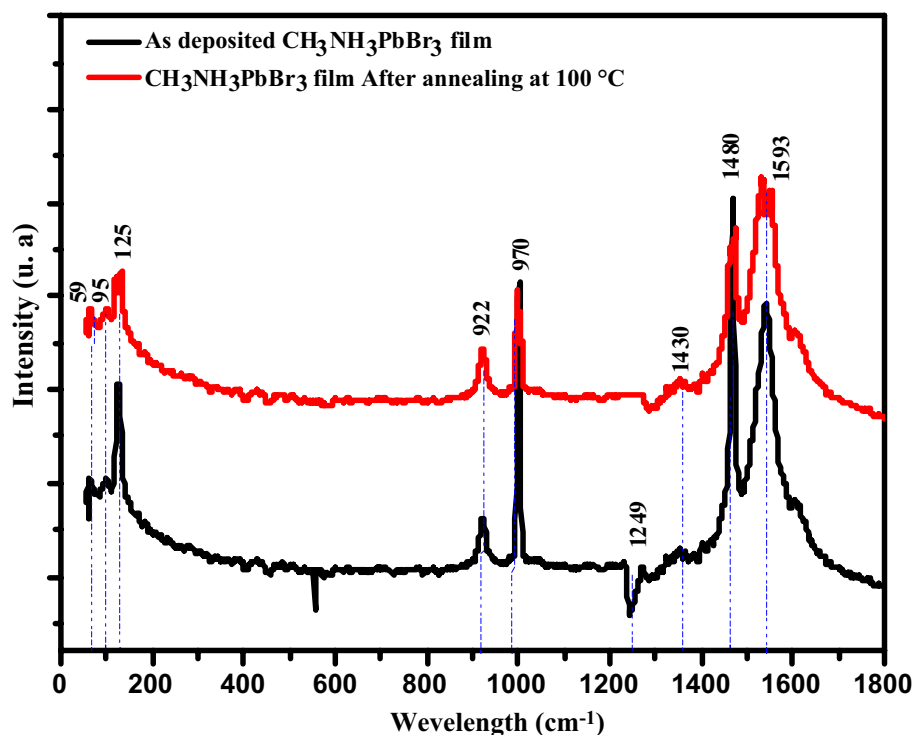


Table 2 Symmetry, Character, Frequency, and Raman Intensity of the Internal Vibrations of perovskite $\text{CH}_3\text{NH}_3\text{PbBr}_3$

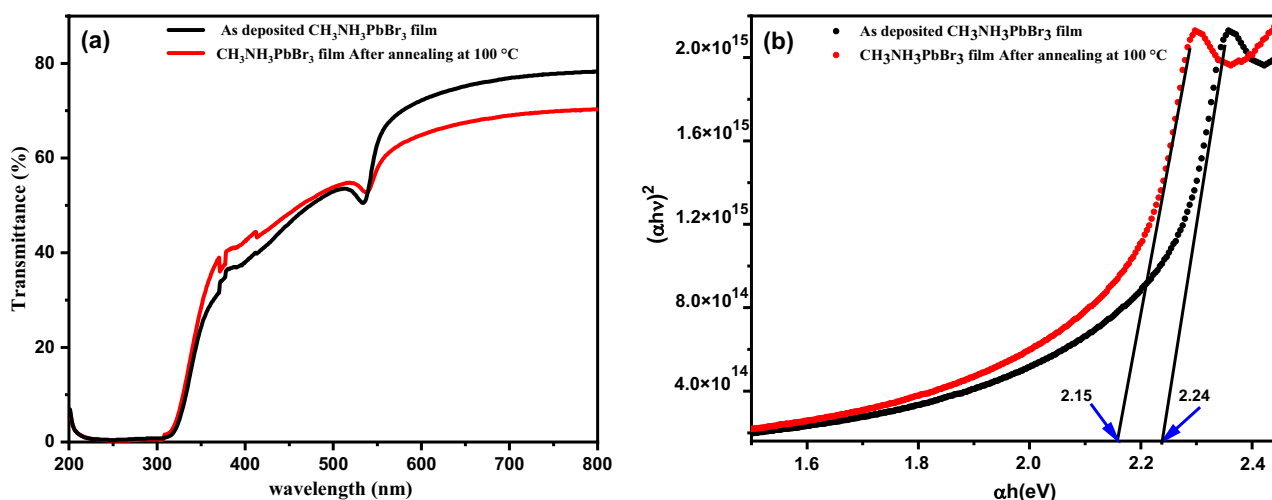
Mode No	Molecular symmetry	Character [58]	Frequency (cm^{-1})
57	E	liber/trans	64
62	A_1	spin	95
81–84	A_1	CH_3NH_3^+ rocking	125
85–88	E	sym.C-N stretch	321
97–100	E	sym. CH_3 deformation	924
101–108		asym. CH_3 deformation	1001
117–120		asym. NH_3 deformation	1370
		NH_3 twisting	1403
			1465
			1544
			1614

associated frequencies. Different symmetry types, such as E and A_1 , categorize the vibrational modes obtained, corresponding to specific molecular motions including rocking, stretching, and deformation of the organic CH_3NH_3^+ cation and inorganic framework. Notably, librational and translational modes in the low-energy frequency range from 57 cm^{-1} to higher energy modes above 1400 cm^{-1} are primarily associated with internal vibrations of the cation. The observed Raman activity indicates significant interactions within the material's structure, reflecting both the dynamics of the organic components and the stability of the inorganic octahedral framework.

5 Optical properties

Figure 7a shows a transmittance of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ thin perovskite films before and after annealing. The evolution of UV–visible spectra is clearly influenced by air annealing treatment. The as-deposited film shows a good absorption in the visible range, especially between 400 and 750 nm. After annealing, the film exhibits a slight increase in transmittance from 70 to 80%. This is due to the air annealing that facilitates grain growth, removes residual solvents and organic components, leading to a more uniform film morphology, as confirmed in SEM analysis in Sect. 3.1. Furthermore, the smoother surface and reduced grain boundary density, resulting from annealing, help to minimize the light scattering and trapping states that contribute to greater transparency [42, 43].

According to the Tauc plot formula, the bandgap analysis of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ thin films before and after annealing (Fig. 7b) reveals a clear change in optical properties due to the annealing process. The plot presents the squared product of the absorption coefficient $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$), indicating a direct bandgap of the films. Before annealing, the extrapolation suggests a bandgap of approximately 2.24 eV. After annealing treatment, the bandgap slightly shifts toward 2.15 eV due to the formation of new chemical bonds between methylammonium cation and PbBr_6 octahedra, which alters the electronic structure. This bonding change can reduce the bandgap by enhancing the interaction between the organic and inorganic components, facilitating charge

**Fig. 7** **a** Transmittance, and **b** bandgap curve $(\alpha h\nu)^2$ versus $h\nu/\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite films before, and after annealing at 100 °C

transport at lower energy states [44]. Therefore, the annealing treatment can improve the film crystallinity and decrease the defect density, affecting the electronic band structure and leading to reduced scattering and absorption, as reported previously [43].

5.1 Stimulate sunlight photodetector

The photoresponsivity ($I_{\text{Light}}/I_{\text{Dark}}$) and sensitivity ($(I_{\text{Light}} - I_{\text{Dark}})/I_{\text{Dark}}$) over applied voltage of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ films by stimulated sunlight lamp are presented in Fig. 8. An Ohmic contact (Cu) was used during irradiation with sunlight that allows efficient charge transport, which is essential for high-performance photodetectors. The formation of an Ohmic contact between Cu and $\text{CH}_3\text{NH}_3\text{PbBr}_3$ thin films is attributed to a favorable energy barrier for charge carriers [45–47]. The work function of Cu ($\varphi_{\text{Cu}} = 4.7$ eV) being lower than that of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ film ($\varphi_{\text{CH}_3\text{NH}_3\text{PbBr}_3} = 4.9$ eV) that facilitates the ohmic junction enhances the charge mobility and reduces the recombination losses [47]. It was found that the annealed $\text{CH}_3\text{NH}_3\text{PbBr}_3$ film at 100°C exhibits both the highest photosensitivity and photoresponsivity that reached maximum values of 520 and 490 at 3.91 V and 4.7 V, respectively, due to the large grain size and low defects [47].

Figure 9 presents the dynamic photo-response over time as the current–voltage (I–V) curves as well of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ films under several dark and illumination alternating cycles using a stimulated sunlight

of (320–800) nm wavelength between voltage ranges from (0 to 5) V with the interval of 30 s. For the as-deposited $\text{CH}_3\text{NH}_3\text{PbBr}_3$ film, the current is relatively low and stable at approximately (2–2.5) mA, as seen in Fig. 8a, indicating a limited photoconductivity due to the very low capacity to generate charge carriers under light. In contrast, the annealed $\text{CH}_3\text{NH}_3\text{PbBr}_3$ film at 100°C , the current increases significantly and reaches a maximum value above 10 mA, which exhibits a clear improved and reversible photoconductive response. Whereas, the current rapidly decreases to low levels in dark. The high photoconductive response of the annealed film can be attributed to improved film crystallinity, reduced surface or bulk defects, and increased lifetime of charge carriers. This is consistent with that obtained by (Stranks et al. 2013.,) [48] that have found that thermal annealing is very effective for improving the morphological and enhancing their photodetector performance of perovskite films. It is noted that (I–V) curves are linear, indicating a good Ohmic contact between the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ films and the Cu electrodes (Fig. 9b). The current–voltage (I–V) curves showed that the as-deposited $\text{CH}_3\text{NH}_3\text{PbBr}_3$ film in both the dark and the light exhibit very low currents, confirming their poor photovoltaic performance (Fig. 9b). Conversely, the annealed $\text{CH}_3\text{NH}_3\text{PbBr}_3$ film at light exhibits a high and linear conductivity, while the dark current film remains very low over the entire voltage range. Thus, the annealing treatment at 100°C was found to be essential for improving the optoelectronic properties of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ film by increasing

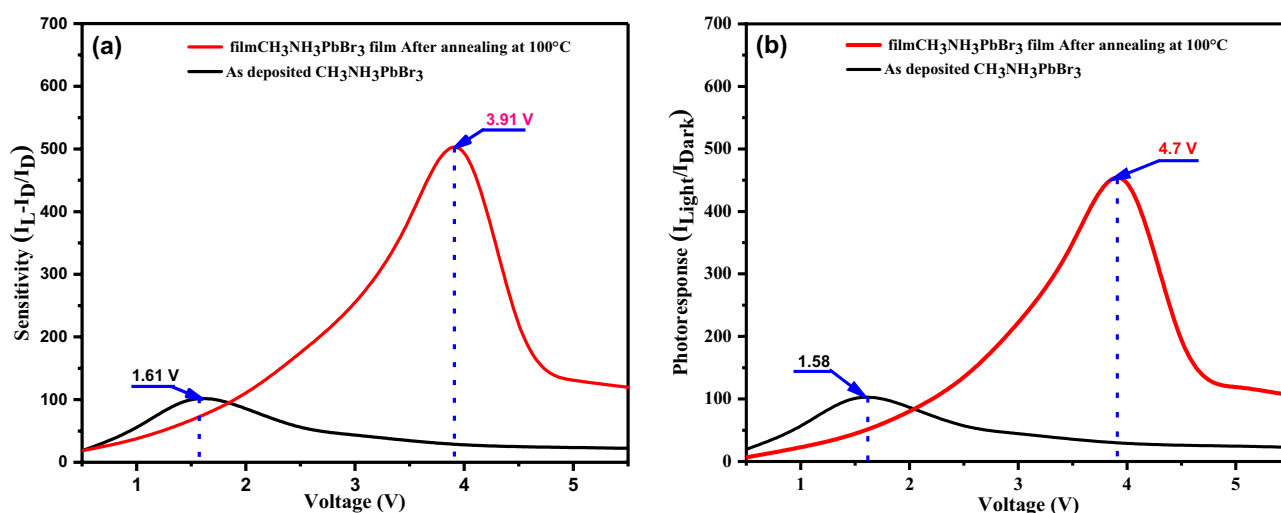


Fig. 8 a Sensitivity and b Photo-response of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ films before and after annealing at 100°C

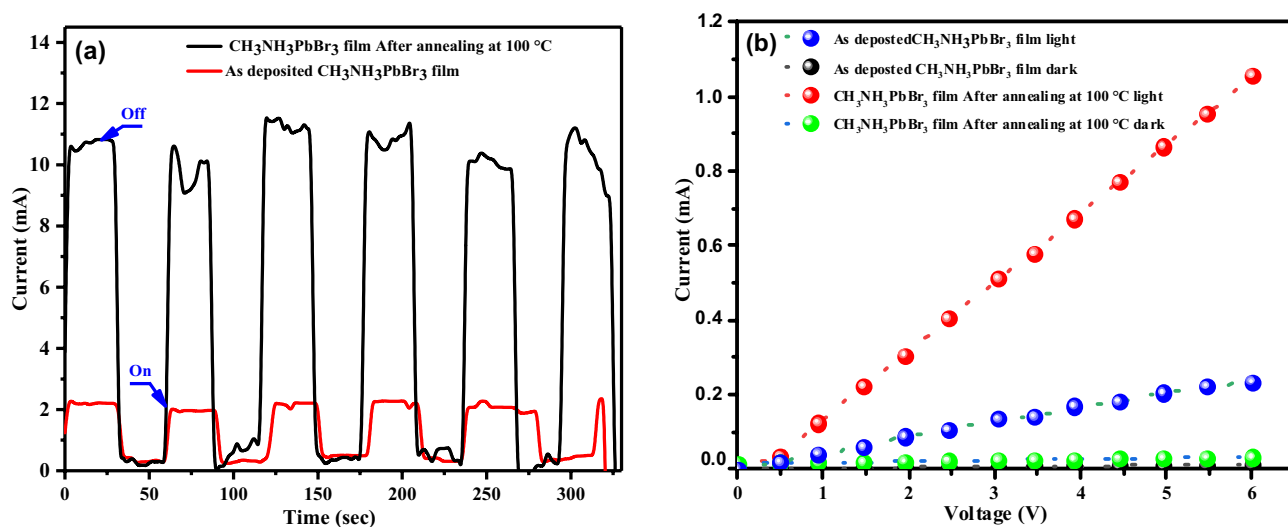


Fig. 9 **a** $I(t)$, **b** $I(V)$ curves of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ film as-deposited and after annealing in the dark and under stimulated sunlight illumination

carrier mobility, reducing recombination, and improving the photoconductive performance of perovskite films (Al-Mousoi et al. 2020.,) [49, 50]

5.2 Photocatalytic degradation of methylene blue (MB)

$\text{CH}_3\text{NH}_3\text{PbBr}_3$ thin films' photocatalytic activity was investigated by measuring the degradation of methylene blue (MB) solution under solar sunlight. The rate of decolorization was recorded with respect to the change in the intensity of the absorption peak in the visible region. The prominent peak was observed at 685 nm, which decreased gradually with the increase in irradiation time of 270 min (each 30 min), indicating that the dye had been gradually degraded. It is observed that the annealed $\text{CH}_3\text{NH}_3\text{PbBr}_3$ film showed higher photodegradation efficiency, and the color disappearance of the MB solution was noticeable compared to the as-deposited $\text{CH}_3\text{NH}_3\text{PbBr}_3$ film. The degradation efficiency was found to increase slightly from 12.67, 15.53, 27.80, 35.23, 36.97, 41.83, 49.63, 70.05, and 78.25%, for 30, 60, 90, 120, 150, 180, 210, and 240 min of irradiation time, respectively, as seen in (Fig. 10b).

Meanwhile, the as-deposited $\text{CH}_3\text{NH}_3\text{PbBr}_3$ film showed only 20% dye degradation after 3 h. Thus, the annealed $\text{CH}_3\text{NH}_3\text{PbBr}_3$ thin film with a large grain and homogeneous surface presents a better degradation of MB than that of the as-deposited

film with a porous surface. Large grains with a high number of grain boundaries play a vital role in the degradation mechanism and increase the active surface sites. (Kaneva et al. 2015.,) [51] found that the formation of films with high defects presents photogenerated holes and promotes the photocatalytic activity.

The degradation kinetics of MB analyzed to reveal the reaction rate of the samples based on the above results. The data were fitted by a first-order kinetic commonly used model to describe the degradation of organic pollutants [52]. Figure 11 shows the kinetics of the degradation reaction of (MB) dye as a function of the irradiation time under solar sunlight of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ films before and after annealing at 100 °C. The first-order rate constant (k) presents a slope of the linear regression between the fluctuations in $(-\ln C_t/C_0)$ and the irradiation time (Fig. 9). The best photocatalytic efficiency after 270 min is obtained with the annealed $\text{CH}_3\text{NH}_3\text{PbBr}_3$ film at 100 °C with a rate constant $k = 0.00526 \text{ min}^{-1}$. It is noted that the photocatalytic efficiency of the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ film annealed at 100 °C is much higher than that of the as-deposited film ($k = 0.00431 \text{ min}^{-1}$). This improvement in the photocatalytic response and the high decolorization of (BM) may be due to the improvement in crystallinity and a large grain size, as observed by XRD and SEM analyses.

Before annealing, the film often has a porous structure with grain refinement and high defects, thus

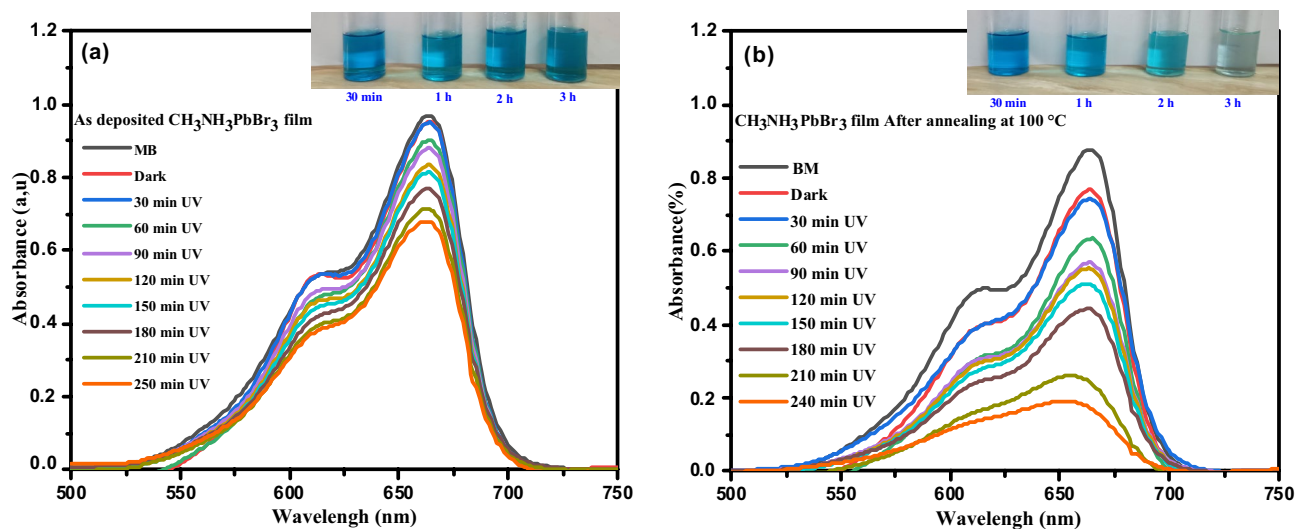


Fig. 10 Photocatalytic performance of $\text{CH}_3\text{NH}_3\text{PbBr}_3$: a) before and b) after annealing at 100 °C over time of MB dye measured using UV–vis spectroscopy

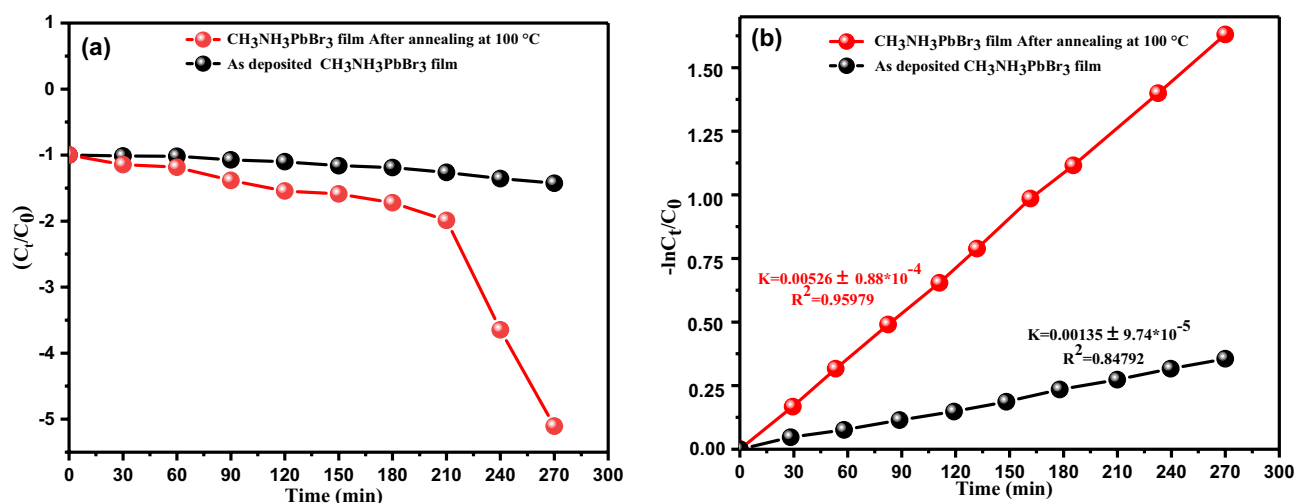


Fig. 11 Corresponding plots for reaction rate constant of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ films before and after annealing at 100 °C thin films

inefficient photodegradation. The annealing treatment at 100 °C increases the grain size and reduces the grain boundaries, which improve the optical properties of the film by reducing light scattering and increasing the charge transport. Furthermore, the annealing can cause a slight shift in energy levels, improving charge separation and transfer to the surface and allowing the photogenerated (electrons/holes) to be more efficiently transported to surface reaction sites, which improves the photocatalytic degradation efficiency [53–55].

The variation of the degradation rate of MB as a function of the exposure time under solar sunlight by perovskite $\text{CH}_3\text{NH}_3\text{PbBr}_3$ thin films before and after annealing at 100 °C, illustrated in Fig. 12. The degradation rate is calculated according to the formula (5). It is evident that the concentration of MB solution under solar sunlight decreases as the decolorization time increases (Fig. 12b). After 270 min, the degradation of the MB is very advanced for the annealed $\text{CH}_3\text{NH}_3\text{PbBr}_3$ film at 100 °C. The percentage of degradation is relatively convergent for the annealed film,

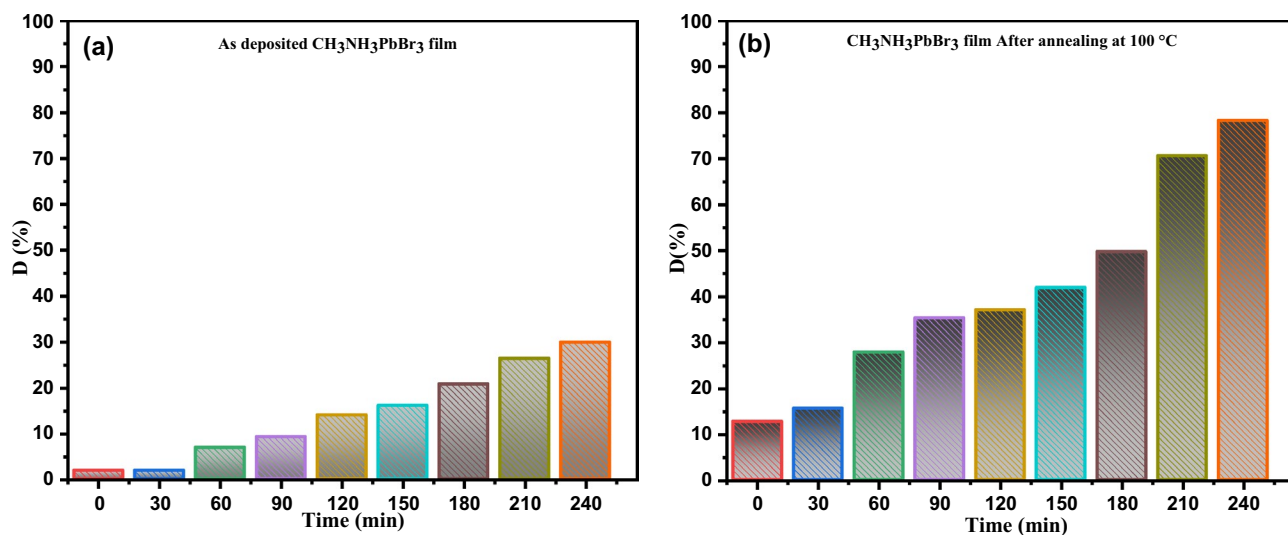


Fig. 12 Variation of degradation rate over time of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ films before and after annealing at 100 °C thin films

while that of the as-deposited $\text{CH}_3\text{NH}_3\text{PbBr}_3$ film shows that the degradation of MB is very low. This is due to the decrease in the bandgap of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ film from 2.24 to 2.15 eV after annealing at 100 °C.

In order to determine the photocatalytic efficiency of the perovskite film treated at 100 °C, we performed the decomposition of methylene blue (MB) over four consecutive cycles. Figure 13a displays the degradation rate of MB over four cycles, showing a high initial photocatalytic activity of about 65% in the second. $\text{CH}_3\text{NH}_3\text{PbBr}_3$ films degrade methylene blue (MB) by

absorbing the light to generate (electron–hole) pairs, which migrate to the surface film and react with water and oxygen, forming highly oxidizing radicals such as $\text{OH}^\cdot$ and $\text{O}_2^{\cdot-}$. These radicals decompose the methylene blue (MB) molecules into less harmful byproducts, as we will see later.

However, the efficiency of the film declines and the degradation rate gradually and significantly decreases over several usage cycles, highlighting the instability of the photocatalytic performance of the film under repeated use, as demonstrated previously. Loss in

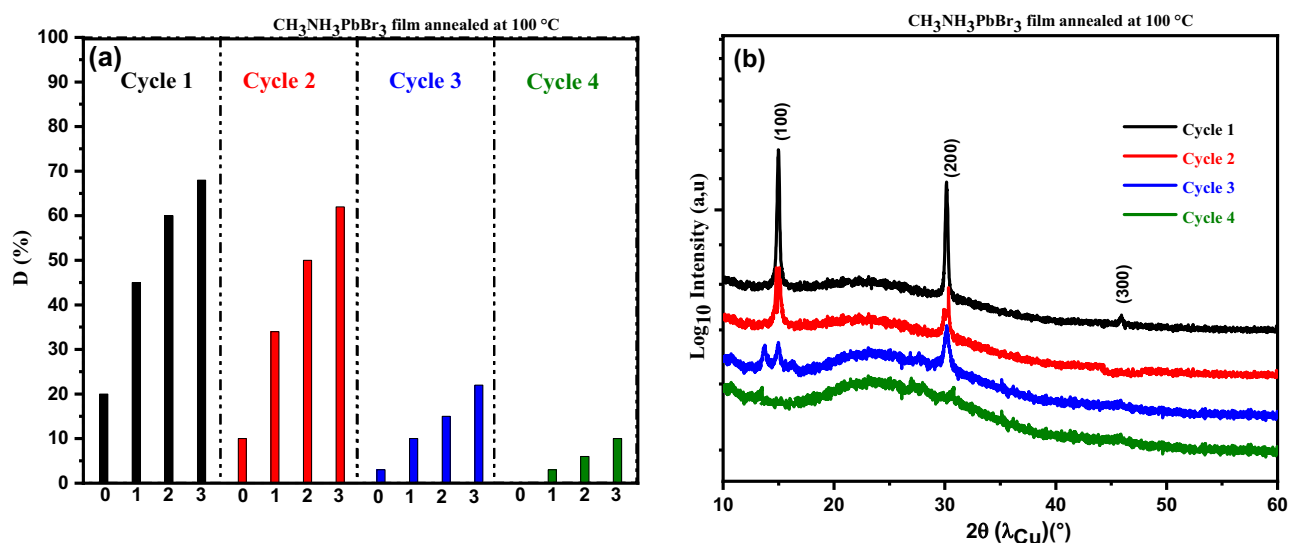
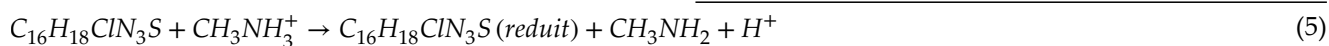


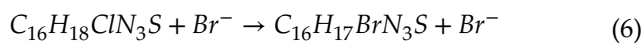
Fig. 13 a Degradation rate of methylene blue (MB), b XRD patterns of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ films annealed at 100 °C thin film after photocatalytic tests over multiple cycles

efficiency is related to the microstructural changes observed in XRD analysis of the film surface after each cycle (Fig. 13b), where the intensity of (100), (200), and (300) diffraction peaks of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite phase significantly decreases from cycle 1 until they disappear completely in cycle 4. This decrease in the XRD peaks intensity is due to the intrinsic instability of the film crystalline structure [56]. Therefore, the loss of photocatalytic efficiency of the film is mainly attributed to the irreversible degradation of the perovskite film, which directly affects its suitability for a long time [57]

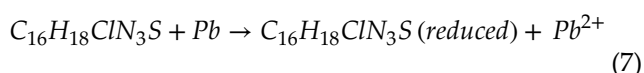
To provide a more comprehensive understanding of the photocatalytic mechanism, methylene blue (MB) degradation experiments using scavengers were conducted. Based on these findings, we propose the following photocatalytic mechanism. For $\text{CH}_3\text{NH}_3\text{PbBr}_3$, the chemical elements (CH_3NH_3 , Pb, Br⁻) can play crucial roles in the degradation of (MB) under solar sunlight during photocatalytic reactions. The degradation of (MB) in the presence of CH_3NH_3^+ (methylammonium) can be achieved by a chemical reduction process as follows:



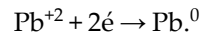
Br⁻ can replace the Cl⁻ in the structure of methylene blue (MB), which can change the reactivity of the molecules and leads to the formation of $\text{C}_{16}\text{H}_{17}\text{BrN}_3\text{S}$, as a following equation:



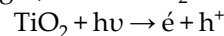
The Pb can also transfer electrons to methylene blue (MB), thereby reducing the dye and oxidizing the lead from Pb to Pb²⁺. This process is a redox reaction in which lead acts as a reducing agent, and methylene blue undergoes reduction. The chemical reaction of Pb and (MB) could be summarized as follows:



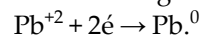
This leads to an increase in the concentration of the liquid lead (Pb²⁺). The addition of a small amount of TiO_2 to the solution can favor the reduction of the lead (Pb²⁺) to Pb⁰, which precipitates out of the solution before catalysis; Pb²⁺ is dissolved in the liquid. After catalysis, it may be reduced, precipitated, adsorbed onto the catalyst, or absorbed in a less mobile form that removes the toxicity of Pb as follows: [59]



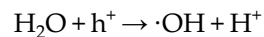
Pb²⁺ gains an electron in the TiO_2 reaction under light, where TiO_2 is activated.



The resulting electrons reduce the lead ions.



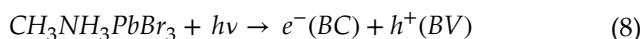
The holes are consumed in the oxidation of water as follows:



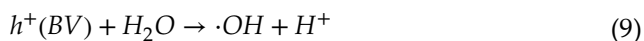
Upon light irradiation, photo-excited electrons from the conduction band of perovskite are preferentially transferred, where they react with dissolved oxygen to generate $\cdot\text{O}_2^-$ as the primary reactive species. Meanwhile, the accumulated holes in the valence band of perovskite oxidize water to produce $\cdot\text{OH}$, which also participate in the MB degradation.

During the photocatalyst degradation under sun solar light, it absorbs photons with energy equal to or greater than its bandgap energy. In addition, within the annealed $\text{CH}_3\text{NH}_3\text{PbBr}_3$ film with a lower Fermi energy level compared to that of as-deposited $\text{CH}_3\text{NH}_3\text{PbBr}_3$ film. As a result, electrons can readily transfer from the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ film conduction band

to the surface of the MB, which significantly inhibits the recombination of electron-hole pairs and facilitates the dyeing of the MB solution. When $\text{CH}_3\text{NH}_3\text{PbBr}_3$ is exposed to sun solar light, the electrons are excited from the valence band (BV) to the conduction band (BC) as seen in the following equations:



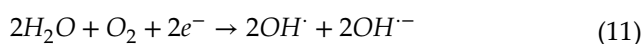
Holes (h^+) are generated in the valence band of oxidized water molecules to form hydroxyl radicals ($\cdot\text{OH}$) as obtained in (Eq. 9).



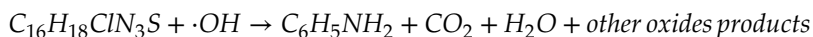
Electrons (e^-) in the conduction band react with dissolved oxygen to produce superoxide ions (O_2^-) (Eq. 10).



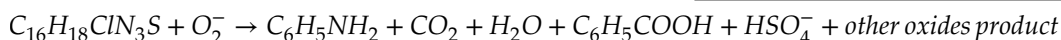
Superoxide ions also can react with water to produce hydroxyl radicals ($\cdot\text{OH}$):



Furthermore, Hydroxyl radicals ($\cdot\text{OH}$) react with Methylene blue ($\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$) to produce aniline ($\text{C}_6\text{H}_5\text{NH}_2$), CO_2 , H_2O , and other oxidation products.



Superoxide (O_2^-) attacks methylene blue (MB), causing its degradation to products CO_2 , H_2O , aniline ($\text{C}_6\text{H}_5\text{NH}_2$), benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$), hydrogen sulfate (HSO_4^-) and other oxidized products:



The enhanced photocatalytic efficiency is schematically described in (Fig. 14). The $\text{CH}_3\text{NH}_3\text{PbBr}_3$ film photocatalyst was irradiated under solar light. In summary, the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ acts by charge separation that leads to access to the transfer of the electron from the valence band to the conduction band, resulting in penetration into VB, which promotes photo-generated charge separation. These separated electrons and holes directly counteract the superoxide anion and hydroxide radicals. Hence, they produce a maximum degradation efficiency of MB. The main role of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ is to produce electron-hole pairs upon exposure to solar light. These electron-hole pairs produce 2OH^- and O_2 that cause the degradation of BM, as illustrated in equations and in (Fig. 14)[60–61].

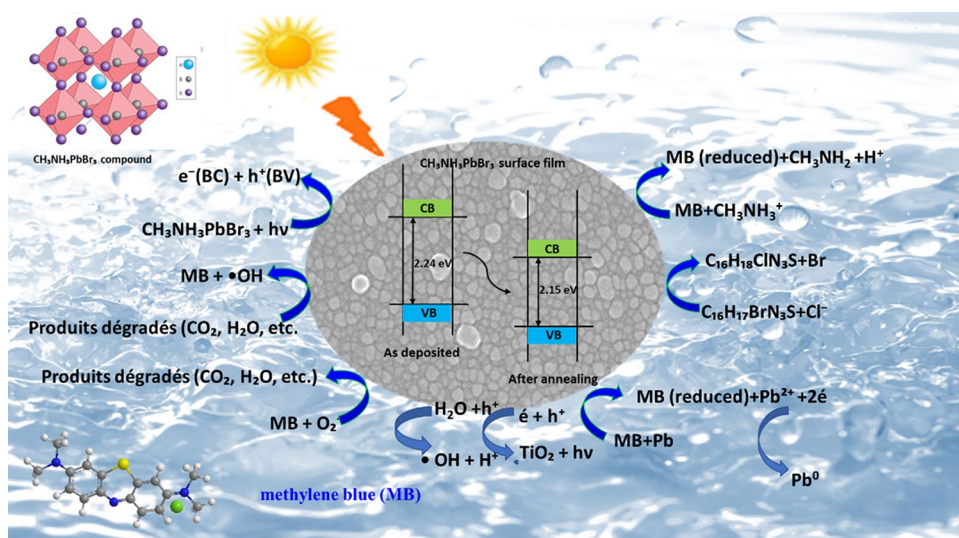
6 Conclusion

The $\text{CH}_3\text{NH}_3\text{PbBr}_3$ films were prepared through dip

coating technique. The study delivers comprehensive insights into the phase structure, chemical composition, and surface morphological characteristics of the synthesized $\text{CH}_3\text{NH}_3\text{PbBr}_3$ film, highlighting the

influence of annealing treatment on this property. The results suggest that the annealing treatment at 100°C can lead to changes in crystalline phases, chemical composition, and crystallite size. As was demonstrated by the results, modifications in absorbance spectra in the visible range are compatible with a slight decrease of bandgap from 2.24 to 2.15 eV, with implications for the photocatalytic performance of the films. The annealed $\text{CH}_3\text{NH}_3\text{PbBr}_3$ film at 100°C showed good protection and high photocatalytic decolonization performance of methylene blue (MB) under solar sunlight after 3 h over different cycles. Thus, the post-annealing $\text{CH}_3\text{NH}_3\text{PbBr}_3$ film presented promising photocatalytic activity under sun solar light for the degradation of the organic polluted water.

Fig. 14 Possible mechanism for the degradation of MB by sun solar light irradiated $\text{CH}_3\text{NH}_3\text{PbBr}_3$ film under sun solar light



Acknowledgments

The authors gratefully acknowledge the support of the Research Center in Industrial Technologies in Algiers, Algeria.

Author contributions

Samia Benhouria: Investigation, Conceptualization, Methodology, Data collection, Analysis, Writing – original draft, Writing – review and editing; Linda Aissani: Supervision, Analysis, Writing – review and editing, Validation; Lamia Radjehi: Supervision, Analysis, Writing – review and editing, Validation; Abdelkader Djalloul: Supervision, Visualization and Validation; Mohamed Farid Benlamnouar: analysis samples, Mohamed Amine Soualili: analysis samples.

Funding

The authors declare that no financial support, grants, or funding were received during the preparation of this manuscript.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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