

Communication

Accessible New Non-Quantum Dot $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ -Based Photocatalysts for Efficient Hole-Driven Photocatalytic Applications

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Abstract: Efficient, low-cost photocatalysts with mild synthesis conditions and stable photocatalytic behavior have always been the focus in the field of photocatalysis. This study proves that non-quantum-dot $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ -based materials, created by a simple method, can be successfully employed as new high-efficient photocatalysts. The results demonstrate that two-dimensional $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ perovskite can achieve over three times higher photocatalytic performance compared to three-dimensional CsPbBr_3 perovskite. Moreover, the photocatalytic performance of $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ can be further improved by constructing a heterojunction structure, such as $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$. $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ can connect well with CsPbBr_3 through a simple method, resulting in tight bonding at the interface and efficient carrier transfer. $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ exhibits notable 5-fold and 10-fold improvements in photocatalytic performance and rate compared to CsPbBr_3 . Additionally, $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ demonstrates superb stable catalytic performance, with nearly no decrease in photocatalytic performance after 7 months ($\text{RH} = 20\% \pm 10$, $T = 25^\circ\text{C} \pm 5$). This study also reveals that the photocatalytic process based on $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ can directly oxidize organic matter using holes, without relying on the generation of intermediate reactive oxygen species from water or oxygen (such as $\cdot\text{OH}$ or $\cdot\text{O}_2^-$), showcasing further potential for achieving high photocatalytic efficiency and selectivity in anhydrous/anaerobic catalytic reactions and treating recalcitrant pollutants.

Keywords: perovskite photocatalysis; two-dimensional $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ -based materials; hole-driven photocatalytic process; stable; high-efficient photocatalysts



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1. Introduction

Currently, non-metallic and metal oxide (sulfide) semiconductor materials are selected as the most commonly used photocatalysts in the photocatalysis field [1,2]. For these photocatalysts, a high-temperature annealing process is usually required, and the wide band gap for the most efficient oxide materials only allows them to be effectively used in the ultraviolet light range [3]. In addition, proper control of the nanoparticle size is also necessary. For example, the titanium dioxide (TiO_2) particles should be controlled at the 10–30 nm level to ensure a high specific surface area for achieving high photocatalytic performance [4]. Moreover, superoxide anions or hydroxyl intermediate radicals are usually required to ensure the smooth progress of the photocatalytic process driven by these oxide catalysts, the performance of which often depends on the level of dissolved oxygen concentration or water molecules [5]. In the photocatalysis field, the development of new photocatalysts with a high efficiency, low cost, easy synthesis, non-dependence of intermediate active radicals, and stable photocatalytic behavior has always been a focus of photocatalytic studies [6].

Due to their outstanding photophysical characteristics, perovskite materials have emerged as an effective light-absorbing layer for solar cells, and their solar cells can achieve a photoelectric conversion efficiency of over 26% [7]. As suitable candidates for efficient

photocatalysts, the prime characteristics of photo-generated carriers and the transmission of carriers are effective [8,9]. Among perovskites, the cesium lead bromide (CsPbBr_3) perovskite with the suitable tolerance factor of 0.82 is well maintained as the perovskite structure [10–13]. Recently, some attempts have been made to use CsPbBr_3 nanocrystals in the form of quantum dots as different kinds of photocatalysts. During organic reactions, the CsPbBr_3 quantum dot, when used as a catalyst, has been identified to accelerate bond formations, with a high yield [14]. As a useful organic pollutant degradation photocatalyst, the CsPbBr_3 quantum dot can effectively degrade the organic compound of 2-Mercaptobenzothiazole [15]. Additionally, the construction of CsPbBr_3 -based heterostructures, such as $\text{CsPbBr}_3/\text{TiO}_2$, has been adopted to reduce the nonradiative recombination of carriers, ultimately improving the photocatalytic performance of CsPbBr_3 [16,17].

To date, studies on CsPbBr_3 or its heterostructure photocatalysts mainly focus on the CsPbBr_3 quantum dot due to its improved stability and quantum size effect [18–22]. Nevertheless, the preparation of quantum dots often involves issues with the cost of preparation and controlling the yield of the high-quantity nanocrystals [23–26]. Additionally, most heterojunction-structured CsPbBr_3 photocatalysts are still involved with a high-temperature preparation process ($>300^\circ\text{C}$) due to high-temperature-annealed materials, such as TiO_2 [27]. Meanwhile, there are some problems, such as the fact that the surface ligands of quantum dots, such as oleyl amine and oleic acid, can eliminate the holes contributing to the photocatalytic processes, or unwanted or uncontrolled photoreactions can occur, ultimately leading to decreased perovskite stability and limited photocatalytic performance [28]. To face these issues, it is valuable to further explore new-structured and new-type perovskites for photocatalytic applications.

In this study, non-quantum-dot, $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ -based perovskite materials were investigated as new-type photocatalysts for efficient hole-driven photocatalytic applications. The results indicate that these photocatalysts can be easily obtained at low temperatures (140°C) by a simple solution method. Compared with CsPbBr_3 , $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ photocatalysts can achieve 3-fold and 7-fold improvements in photocatalytic performance and rate. Moreover, by constructing the $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ heterostructure structure, due to the tight bonding of interface and suitable valence band, the photocatalytic performance and rate can be further increased by 5 times and 10 times. Additionally, $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ photocatalysts show excellent photocatalytic stability, with almost no decrease in photocatalytic performance after 7 months in the air and after cyclic catalytic tests. Additionally, the results also reveal that the photocatalytic process based on $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ can be directly driven by holes, without relying on the generation of intermediate reactive oxygen species generated from water or oxygen (such as $\cdot\text{OH}$ or $\cdot\text{O}_2^-$), which exhibit further potential for achieving the high photocatalytic efficiency and selectivity.

2. Results and Discussion

In this study, perovskite photocatalysts were synthesized by a simple solution evaporation method. The details of these processes are shown in the Supplementary Materials. The schematic of preparation for CsPbBr_3 , $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ and $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ perovskite photocatalysts is shown in Figure 1. Taking $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ as an example, CsCl and PbI_2 (molar ratio of 2:1) are added to dimethyl sulfoxide (DMSO) to prepare the solution, and the pre-prepared non-quantum-dot CsPbBr_3 crystals are subsequently dropped into the solution. The $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ photocatalyst can be created by evaporating the solution at a temperature of 140°C .

The XRD measurement was used to detect the crystal structure obtained by the solution evaporation method. As shown in Figure 2a, the diffraction peaks at $2\theta = 15.21^\circ$, 21.49° , 26.34° , 30.37° , and 34.19° corresponded to the (001), (110), (111), (002), and (210) crystal planes of CsPbBr_3 perovskite, comprising the standard cards of CsPbBr_3 perovskite (PDF # 18-036). The XRD patterns of $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ and mixed-dimensional $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ perovskite are shown in Figure 2b. The diffraction peaks of XRD patterns at $2\theta = 9.07^\circ$, 21.77° , 27.60° , and 32.35° correspond to the (002), (110), (105), and (202) crystal planes

of $\text{Cs}_2\text{PbI}_2\text{Cl}_2$, which is consistent with our early research. The XRD pattern of mixed compounds is shown in Figure 2b. As demonstrated by the comparison of XRD patterns in Figure S1, the characteristic diffraction peaks representative of $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ and CsPbBr_3 in the $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ compounds shift towards lower and higher angles, respectively. This indicates that the partial substitution of Cl in CsPbBr_3 and Br in $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ may have occurred during the synthesis of $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ compounds.

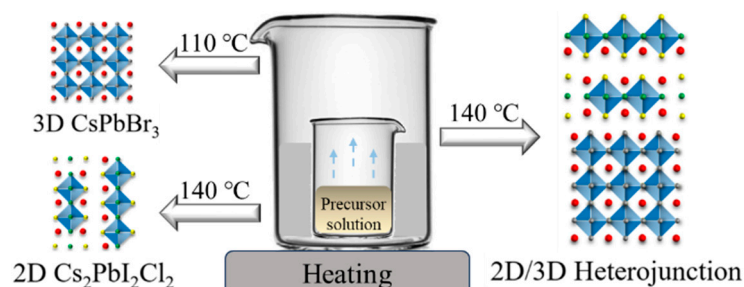


Figure 1. The schematic of preparation for CsPbBr_3 , $\text{Cs}_2\text{PbI}_2\text{Cl}_2$, and mixed-dimensional $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ perovskite photocatalyst.

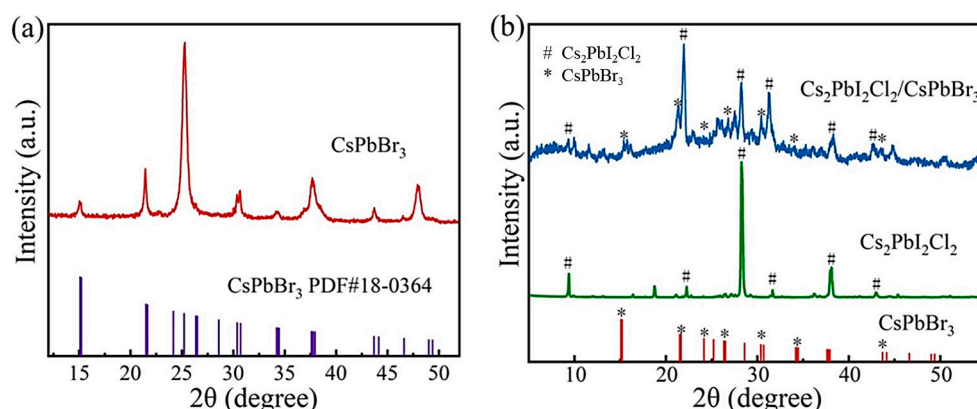


Figure 2. (a,b) The XRD patterns of CsPbBr_3 , $\text{Cs}_2\text{PbI}_2\text{Cl}_2$, and $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ crystals.

To observe the CsPbBr_3 , $\text{Cs}_2\text{PbI}_2\text{Cl}_2$, and mixed-dimensional $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ crystals, scanning electron microscopy (SEM) was performed. It can be observed that the CsPbBr_3 crystals have a bulk shape (Figure 3a), and the $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ crystals display a sheet-like accumulation (Figure 3b). After combining the two types of crystals, it was detected that the crystals had a clear sheet-like shape, but the CsPbBr_3 crystals were not clearly observed (Figure 3c). To further identify the combination of two crystals, high-resolution transmission electron microscopy (HRTEM) was used. As observed from the results (Figure S2a,b), it can be seen that the $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ crystals have a platelike shape, and the dark spots are distributed on the plane of platelike crystals. The lattice fringes observed from the microregion of $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ crystal (Figure 3d) displayed interplanar d-spacings of 2.88 Å and 4.07 Å (Figure 3e), which was consistent with the lattice parameters of the (200) and (110) planes for the two-dimensional $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ crystal. Meanwhile, the interplanar d-spacings of 2.97 Å for the (200) plane of the CsPbBr_3 crystal were also observed from the TEM pattern shown on the right side of Figure 3e. The lattice misfit values of (200) of $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ and (200) of CsPbBr_3 were calculated using $\delta = (d(200)_{2D} - d(200)_{3D}) / d(200)_{3D}$ (Figure 3f). The lattice misfit value was calculated as 3% (<5%), which conveniently formed the coherent interface between the different crystal structures according to the semi-coherent dislocation theory [29,30]. The small difference in the d-spacings of two crystals implies the small interfacial energy between (200) of $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ and (200) of CsPbBr_3 , which is beneficial for their connection. As a result, the interface of $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ and CsPbBr_3 structures showed a tight connection, and the lattice structures displayed a smooth transition from the (200) of $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ to (200) of CsPbBr_3 .

(Figure 3e,f). Such a tight connection and smooth transition at the interface between $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ and CsPbBr_3 would effectively reduce the interface carrier transport barrier and facilitate the smooth transmission of photocarriers, thereby reducing the probability of non-radiative recombination and helping to achieve a high photocatalytic performance. As evidenced by XRD and HRTEM results, the $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ mixed-dimensional heterojunction crystal was successfully obtained through a simple solution process.

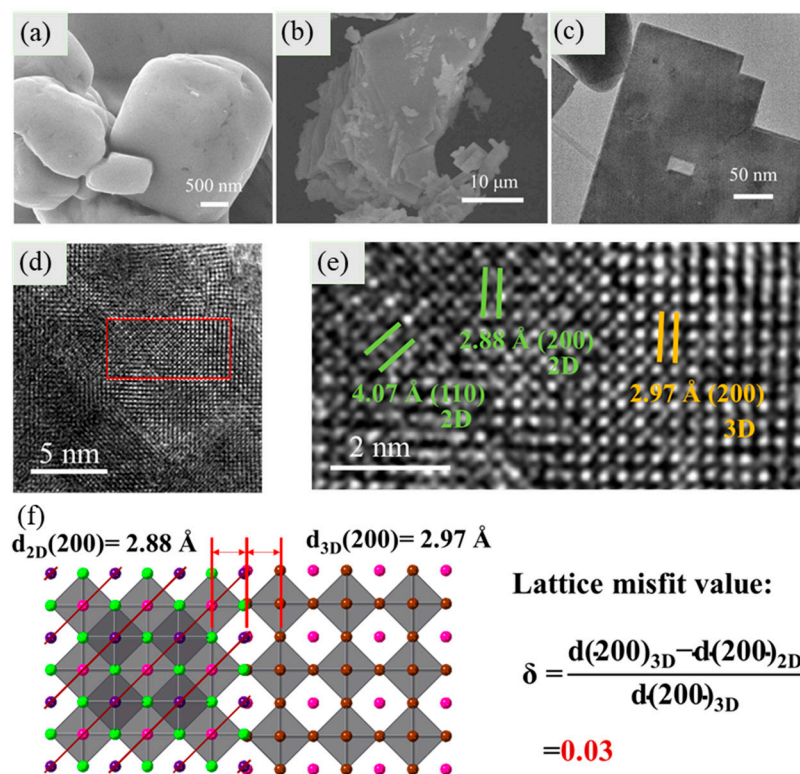


Figure 3. SEM images of (a) CsPbBr_3 , (b) $\text{Cs}_2\text{PbI}_2\text{Cl}_2$, and (c) $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ catalysts; (d) HRTEM results of $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ photocatalyst crystals; (e) The partial area enlarged pattern extracted from (d); and (f) schematic diagram of crystal structure arrangement of $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ and the lattice compatibility.

The optical absorption range and bandgap widths of the CsPbBr_3 , $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ and $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ heterojunction crystalline materials were assessed using ultraviolet–visible absorption spectroscopy (UV–Vis) and ultraviolet–visible diffuse reflectance spectroscopy (UV–Vis DRS). The UV–Vis results revealed that the absorption cutoff edge of CsPbBr_3 at approximately 560 nm, while the presence of CsPbBr_3 extends the cutoff edge of $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ from 460 nm ($\text{Cs}_2\text{PbI}_2\text{Cl}_2$) to around 500 nm (Figure 4a). By fitting curves using the Tauc Plot method in the UV–Vis DRS test, the bandgaps of CsPbBr_3 , $\text{Cs}_2\text{PbI}_2\text{Cl}_2$, and $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ crystalline materials were determined to be 2.24 eV, 2.87 eV, and 2.54 eV, respectively (Figure 4b).

To evaluate the photocatalytic performance of the CsPbBr_3 , $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ and $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ as photocatalysts, the representative organic pollutant Rhodamine B was selected as the standard material. Additionally, the change in the absorbance of the Rhodamine B solution under the simulated sunlight illumination (AM 1.5 G) was used to judge the photocatalytic performances (Figure 5a, where C_0 , A_0 , C , and A represent the concentration and absorbance before and after degradation, respectively). The results of sampling every 2 min displayed that, without any photocatalyst, the organic matter showed no decomposition after 10 min under the light exposure. For the CsPbBr_3 -catalyzed case, only a ~10% and ~20% degradation of organic matter occurred during the relatively high catalytic rate stage after 2 and 4 min. In contrast, the $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ catalyst degraded 36.4 and

67.8% of the organic matter within the same time, which showed that the improvement in performance was at least triple. Impressively, $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ degraded 81.8% and 97.3% of the organic matter after 2 and 4 min, and all organic matter was degraded within 6 min. Although the UV–Vis results showed that $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ and $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ possessed a narrower light absorption range compared to CsPbBr_3 , they could exhibit an improvement in photocatalytic performance of 3–8 times.

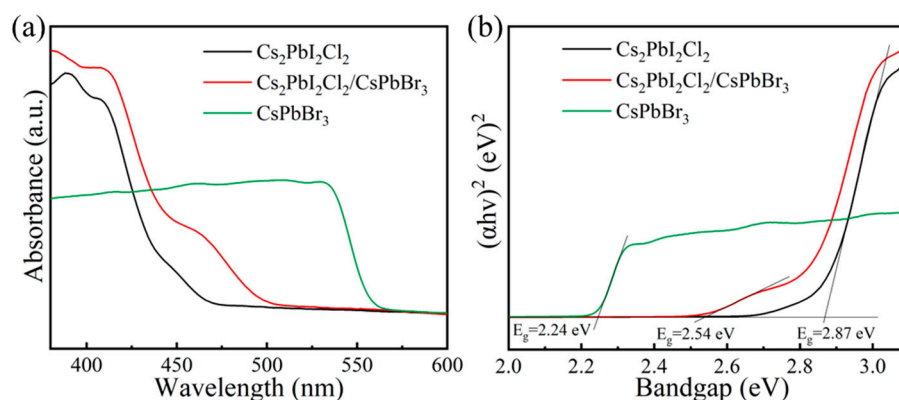


Figure 4. (a) UV–Vis and (b) UV–Vis DRS results of CsPbBr_3 , $\text{Cs}_2\text{PbI}_2\text{Cl}_2$, and $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ photocatalysts.

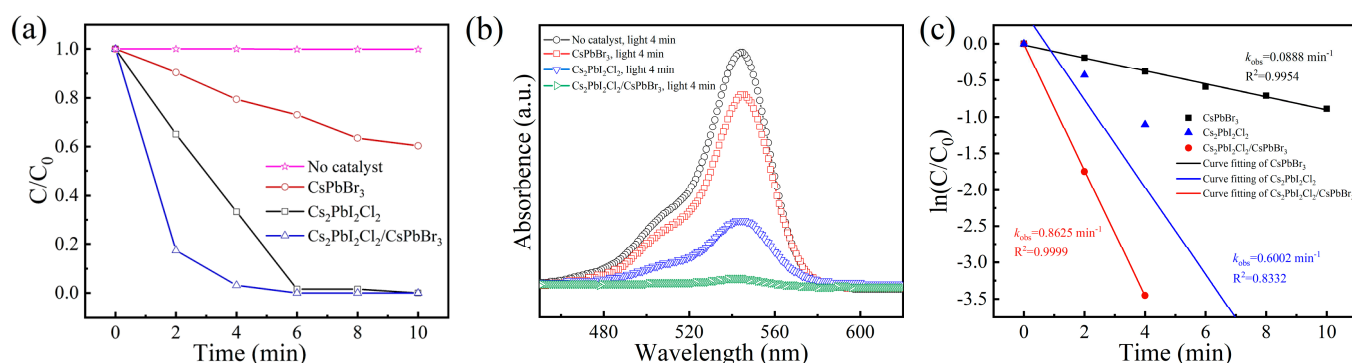


Figure 5. (a) Photocatalytic performance tests of CsPbBr_3 , $\text{Cs}_2\text{PbI}_2\text{Cl}_2$, and $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ photocatalysts; (b) UV–Vis absorption of organic solution without and with catalysis by CsPbBr_3 , $\text{Cs}_2\text{PbI}_2\text{Cl}_2$, and $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ after 4 min; (c) reaction rates of CsPbBr_3 , $\text{Cs}_2\text{PbI}_2\text{Cl}_2$, and $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ fitted by using first–order kinetics.

This enhancement in performance could also be deduced from the UV–Vis results after 4 min (Figure 5b). The solution catalyzed by CsPbBr_3 exhibited strong absorption peaks of organic matter, while the $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ -based solution showed an evident decrease in absorption peaks, and the $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ -based solution showed very weak absorption peaks. Furthermore, the degradation rates of the samples were simulated using first-order kinetics, as shown in Figure 5c. According to the simulating results, the degradation rate of CsPbBr_3 was 0.089 min^{-1} . In contrast, the degradation rates for $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ and the $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ heterojunction structure could reach 0.600 min^{-1} and 0.863 min^{-1} , exhibiting almost a 7–10 times higher photocatalytic rate. In order to better estimate $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ -based photocatalytic performance, the TiO_2 with a 20 nm particle size possessing a relatively high catalytic performance and CsPbBr_3 were selected to construct the heterojunction photocatalyst for comparison (Figure S4). It can be observed that within 4 min, 35% of the organic matter was not catalyzed by the $\text{TiO}_2/\text{CsPbBr}_3$ photocatalyst, and all the organic matter could not be completely catalyzed by $\text{TiO}_2/\text{CsPbBr}_3$ after 10 min. Meanwhile, all Rhodamine B was degraded by the $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ -based photocatalysts within 6–10 min, which implied a high-efficient photocatalytic performance of $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ -based photocatalysts, especially for the $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ heterojunction photocatalyst.

Furthermore, the photogenerated carrier transfer characteristics of the $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ heterojunction crystals were explored through X-ray photoelectron spectroscopy (XPS) and steady-state photoluminescence (PL) measurement. The XPS measurements (Figure 6a) show that the valence band maximum (EVB) for $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ and CsPbBr_3 are at 1.84 eV and 1.07 eV, which suggests that a suitable band offset exists between $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ and CsPbBr_3 perovskite. As observed from PL measurements (Figure 6b), compared to the fluorescence peak of CsPbBr_3 , the peak of the $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ heterojunction exhibited a significant increase in fluorescence intensity. This means that the non-radiative recombination of photogenerated carriers in $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ were more effectively reduced, which was beneficial for providing more active electrons and holes to improve photocatalytic efficiency.

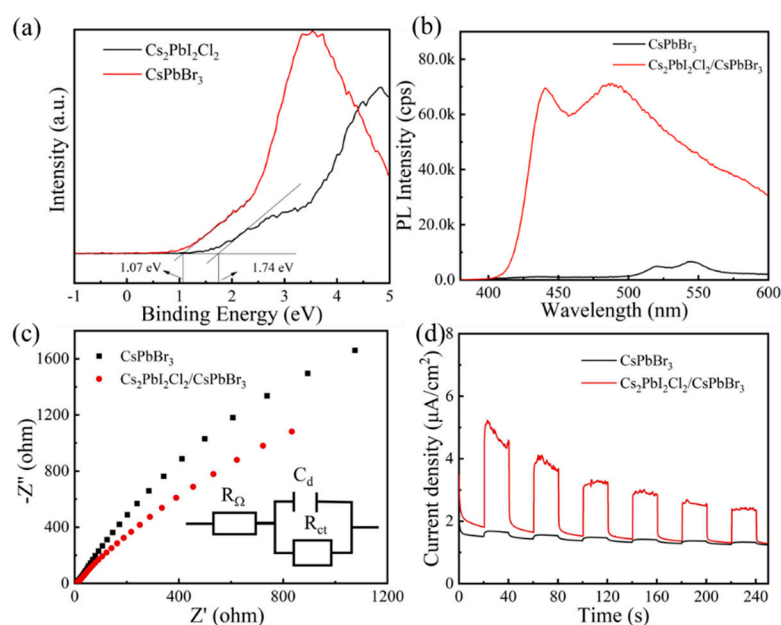


Figure 6. (a) XPS, (b) PL, (c) EIS and (d) transient photocurrent response measurements of CsPbBr_3 and $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ photocatalysts.

To identify carrier mobility, electrochemical impedance spectroscopy (EIS) tests were performed. The results show that the $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ powder exhibited a smaller radius of curvature compared to CsPbBr_3 powder (Figure 6c) and $\text{TiO}_2/\text{CsPbBr}_3$ powder (Figure S5a). This indicates that the $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ powder heterojunction material possesses lower carrier transfer resistance, facilitating more rapid and efficient carrier transfer. The results from transient photocurrent response tests demonstrated that the $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ heterojunction could generate a higher current density than that of CsPbBr_3 (Figure 6d) and $\text{TiO}_2/\text{CsPbBr}_3$ (Figure S5b), further proving the advantage of $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ heterostructure in carrier transfer and transport. When analyzing our previous research, the high photocatalytic performance of $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ should be attributed to the reduced non-radiative recombination, the tight connection of heterojunction structure interface (Figure 3), and the matched energy level (Figure 6a). The rapid and efficient carrier transfer will reduce the probability of non-radiative recombination of holes and electrons, thereby facilitating the participation of more photo-generated active electrons and holes in accelerating photocatalytic processes.

To further our understanding of the photocatalytic mechanisms generated by the $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$, free radical capture experiments were conducted (Figure 7a). Methanol (MT), isopropanol (IPA), and p-benzoquinone (p-BQ) were adopted as the holes (h^+), and hydroxyl radicals ($\cdot\text{OH}$) and superoxide radicals ($\cdot\text{O}_2^-$) were adopted as free radical scavengers, which usually participate in the photocatalytic process [31,32]. According to the results, it could be seen that after 4 min, the degradation rates of organic matter were

decreased from 97.3% to 93.8% and 94.4%, respectively, after the addition of IPA and p-BQ scavengers, which showed no significant effect on the degradation processes. This indicated that $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ were not the primary active species in the photocatalytic reaction driven by $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$. When MT was added, the degradation rate was significantly decreased to 5.2%, successfully inhibiting the degradation process. Therefore, in the photocatalytic process driven by $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$, the h^+ should play the crucial role in the degradation of organic matters.

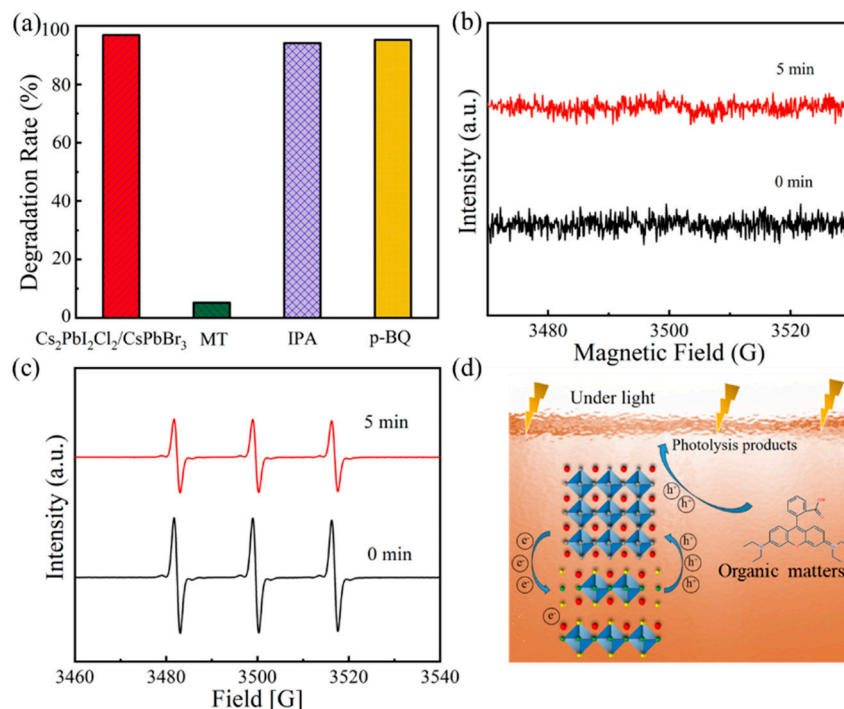


Figure 7. (a) Free radical capture tests for $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ photocatalysts; (b,c) ESR for $\cdot\text{O}_2^-$ generation and h^+ generation for $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ photocatalysts; and (d) schematic diagram of $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ photocatalytic mechanism of organic matters.

Moreover, electron spin resonance (ESR) tests were further performed to validate the crucial role of h^+ and $\cdot\text{O}_2^-$ formed by oxygen/electronics during the photocatalytic processes driven by $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$. In the electron spin resonance detection of $\cdot\text{O}_2^-$ generated from electronics, as shown in Figure 7b, no ESR fluctuation signal appeared under dark conditions and after 5 min of illumination, suggesting that $\cdot\text{O}_2^-$ was indeed not an active radical species participating in the photocatalytic process. This means that the dissolved oxygen in solution is not an essential requirement to ensure that $\cdot\text{O}_2^-$ drives the $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ -based photocatalytic process. To validate the role of photogenerated h^+ , the 2,2,6,6-tetramethylpiperidinoxy (TEMPO) additive was chosen as the capture agent (Figure 7c). As evidenced by the results, under the dark conditions, a high signal peak of TEMPO was detected. When the $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ heterojunction material generated h^+ under illumination for 5 min, the h^+ neutralized with TEMPO, resulting in a significant decrease in the TEMPO signal. These results indicate that the generation of h^+ is the main factor affecting the photocatalytic reaction driven by $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ (Figure 7d). Hence, the dissolved oxygen and water molecules are not necessary to form the $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ intermediate active radicals that guarantee the proceeding of the photocatalytic process. For the hole-driven photocatalytic processes of $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$, it can provide a high-efficient photocatalytic performance due to avoiding energy loss, benefiting from the absence of the need to form $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ intermediate radicals. Meanwhile, the hole-direct-driven catalytic process of $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ -based photocatalysts usually has a high oxidation capacity and exhibits a reduction in side reactions, which are very suitable for

treating recalcitrant pollutants or the catalytic applications of anhydrous and anaerobic organic chemical reactions.

Furthermore, the $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ photocatalyst was proven to possess an excellent photocatalytic stability. The performance stability of the $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ photocatalyst was evaluated through the cyclic catalytic performance and environmental stability tests. The results of the cyclic tests showed that after three cycles, the performance of the $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ photocatalyst only exhibited minor changes within the time period of 2 to 6 min, but the entire catalytic process was still completed within 6 min (Figure 8a). Meanwhile, attributed to the template stabilization effect of stable two-dimensional $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ perovskite structured on three-dimensional CsPbBr_3 structures, the catalytic performance showed almost no change after the catalyst was placed in normal storage environment ($\text{RH} = 20\% \pm 10$, $T = 25^\circ\text{C} \pm 5$) for 7 months (>5000 h) (Figure 8b). This shows that durable high-catalytic-efficiency characteristics are more suitable for the application of organic chemical catalytic reactions. To further identify the stability, accelerated aging tests were performed ($\text{RH} = 60\%$) (Figure S6). After 3 months, a notable attenuation occurred in the reaction rate of CsPbBr_3 -based photocatalytic processes (Figure S6), which decreased from 0.089 min^{-1} to 0.045 min^{-1} (attenuation rate: 49.4%; Figure S7). The stability of $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ exhibited a significant improvement. The reaction rate of $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ -based photocatalytic processes decreases from 0.863 to 0.669 (attenuation rate: 22.4%; Figure S7), and $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ could still complete all of the catalytic reaction within 6–8 min (Figure S6).

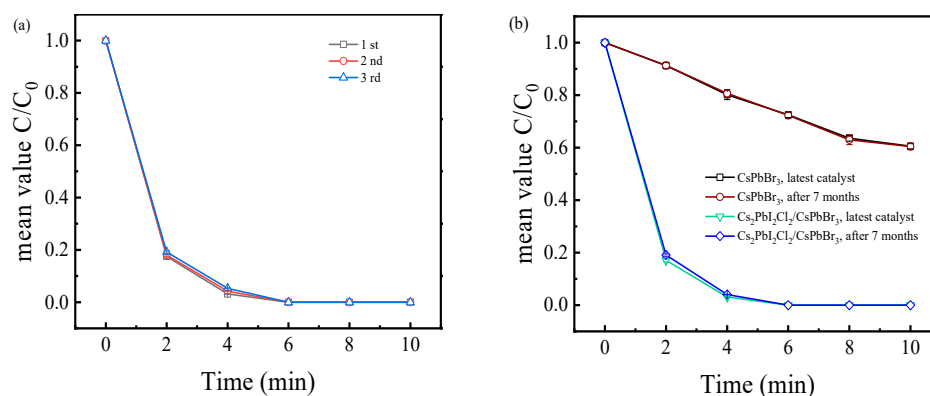


Figure 8. (a) The cyclic recirculation catalytic performance and (b) environmental stability tests for $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ catalysts.

3. Conclusions

In conclusion, the non-quantum-dot, $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ -based perovskites created using our efficient method are proven to be new-type high-efficient photocatalysts. The catalytic performance of $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ is three times better than that of the single CsPbBr_3 photocatalyst, and its catalytic rate is seven times higher. The results confirm that the two-dimensional $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ and CsPbBr_3 may be effectively coupled to create a tightly connected and smoothly transitioning heterojunction structure using a simple method. The tight bonding of the interface and suitable valence band maximum of $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ result in the efficient transfer of carriers and the promotion of photocatalytic process. The photocatalytic performance can be enhanced even further, resulting in a 5-fold and 10-fold increase in catalytic performance and rate. Moreover, $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ can maintain its excellent photocatalytic performance after long-term environmental tests (>5000 h).

Furthermore, it has been observed that these photocatalysts exhibit exceptional photocatalytic efficiency, as they are capable of directly oxidizing organic substances by the action of h^+ ions without the need for the production of intermediary reactive oxygen species derived from water or oxygen (such as $\cdot\text{OH}$ or $\cdot\text{O}_2^-$). Directly harnessing holes for oxidation processes can streamline the steps involved in generating reactive oxygen species, effectively minimizing potential energy waste and the formation of reaction by-

products. The utilization of hole-driven photocatalytic processes is crucial for enhancing the efficiency and selectivity of photocatalytic reactions. Meanwhile, in this photocatalytic process, the strong direct oxidation capacity of h^+ makes $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ -based photocatalysts exceptionally effective in treating difficult-to-degrade pollutants. Such applications amply warrant further exploration and research. In summary, this study presents a simple and attainable method to produce catalyst crystals based on $\text{Cs}_2\text{PbI}_2\text{Cl}_2$, which are not quantum dots. The study also showcases the promising capabilities of these crystals as efficient and long-lasting photocatalysts driven by holes.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/molecules29143249/s1>. Figure S1: XRD patterns of CsPbBr_3 , $\text{Cs}_2\text{PbI}_2\text{Cl}_2$, and $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ crystals; Figure S2: (a), (b) and (c) HRTEM images of $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ photocatalysts; Figure S3: (a) UV-vis absorption of organic solution without and with being catalyzed by CsPbBr_3 , $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ and $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ after 2 min (b) After 4 min (c) After 8 min (d) After 10 min; Figure S4: Photocatalytic performance tests of $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ and $\text{TiO}_2/\text{CsPbBr}_3$ photocatalysts; Figure S5: (a) EIS measurements of $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ and $\text{TiO}_2/\text{CsPbBr}_3$ photocatalysts, (b) transient photocurrent response tests of $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ and $\text{TiO}_2/\text{CsPbBr}_3$ photocatalysts; Figure S6: Accelerated aging testing of $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ and CsPbBr_3 photocatalysts; Figure S7: Reaction rates of $\text{Cs}_2\text{PbI}_2\text{Cl}_2/\text{CsPbBr}_3$ and CsPbBr_3 -based photocatalytic processes fitted by using pseudo-first-order kinetics after accelerated aging tests.

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