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Heterojunction-Type Photocatalytic System Based on Inorganic Halide Perovskite CsPbBr₃

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Summary of main observation and conclusion The heterojunction-type structure has shown significant merits in tuning the optical properties and carrier physics. Inspired by the excellent absorption capability of halide perovskite materials for visible light, a series of CsPbBr₃/TiO₂ heterojunction-type hotocatalyst with various all-inorganic-perovskite/TiO₂ ratios are successfully fabricated by the ligand-assisted reprecipitation (LARP) method. The heterojunction structure extends the light absorption of TiO₂ with good chemical and structural stability. A Pb-O interaction at the CsPbBr₃/TiO₂ interface observed by the XPS and confirmed by the TRPL showing improved interface carrier transport and stability. The heterojunction-type catalyst shows crastically enhanced photocatalytic activity towards the direct oxidation of foluene with O₂ molecule, as an important reaction for organic chemical synthesis. The optimized sample shows an activity of 2356 µmol g⁻¹h⁻¹ at 75 °C, 4 times with the naked CsPbBr₃ nanocrystals, and 3 times the bare TiO₂. Based on the investigation with trapping agents, a reaction mechanism is hence proposed suggesting that the photo-generated hole may be involved in the rate-limiting step. This work demonstrates the potential of inorganic halide perovskite-based heterojunction structure for photocatalytic applications.

Background and Originality Content

The halide perovskite materials have gained considerable attention for solar energy conversion since the first report of the ethylammonium lead iodide (MAPbI₃) -sensitized solar cell in 2009.^[1] Due to their unique optoelectronic properties such as long harge carrier lifetime^[2], high absorption coefficient^[3], high charge carrier mobility^[4-5], and flexible band structure engineering^[6-7], with their low processing cost^[8], the halide perovskite materials are promising candidates for highly efficient and costc mpetitive solar conversion devices.^[9] More recently, it has been eported that the halide perovskite materials show unique activities in the photocatalytic conversion of multiple c emicals.^[10]

The all-inorganic CsPbBr₃ perovskite quantum dots/graphene o ide composite for photocatalytic CO₂ reduction reaction was sported by Kuang *et al*, as the first demonstration of inorganic halide perovskite for photocatalytic application.^[11] So far, in Idition to the CO₂ reduction^[12-13], some other reactions have been achieved by photocatalysis with inorganic halide perovskite, such as the degradation of organics ^[14-18], polymerization^[19-20], o ganic synthesis^[21-24]. Selective oxidation reaction plays an essential role in the chemical industry, whereby the photocatalytic oxidation of organic molecules has drawn intensive interest.^[25] The halide perovskite has been studied for the oxidation of benzylic alcohols^[26-27] and C(sp³)-H bond^[28]. However, due to the limited studies on perovskite-based photocatalysis, the successful oxidation reactions are quite limited with limited understanding of reaction mechanisms such as the carrier transport and molecular conversion process in the photocatalytic system. Therefore, improving the carrier separation efficiency and catalytic efficiency is of high importance to the insightful understanding towards the photocatalysis of perovskite material.

Herein, inspired by the excellent absorption of halide perovskite materials, we report a series of CsPbBr₃/TiO₂ (CPB/Ti) heterojunction-type catalysts with various ratios synthesized via the ligand-assisted reprecipitation (LARP) method, and the demonstrates their activity towards the photocatalytic oxidation reaction of toluene. The CPB/Ti heterojunction-type structure is confirmed by transmission electron microscopy (TEM) and X-ray diffraction (XRD). The interaction at the interface of the two components is studied by X-ray photoelectron spectroscopy (XPS). It is verified through the time-resolved photoluminescence (TRPL) that the formation of Ti-O-Pb at the interface improves the photogenerated carrier transport and hence the photocatalytic performance. By tuning the perovskite/TiO₂ ratio, the photocatalytic reaction rate of the direct conversion of toluene

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into benzaldehyde can be optimized with the highest activity 2356 μ mol g⁻¹h⁻¹ achieved by the 6%CPB/Ti, more than 4 times that of the CsPbBr₃ nanocrystals (NCs) and 3 times the TiO₂. The active intermediate species and the reaction mechanism are studied by using trapping agents. This work demonstrates the potential application of CsPbBr₃/TiO₂ heterojunction for photocatalytic organic synthesis.

Results and Discussion

N aterial structure and morphology

The LARP method has been widely adopted for the synthesis [•] Pb-based perovskite NCs^[29], we manage to fabricate CsPbBr₃ perovskite NCs loaded on TiO₂ by LARP method. By dissolving the precursors in dimethylformamide (DMF) with the hexanoic acid d octylamine as ligands, followed with the re-precipitation in toluene, the obtained heterojunctions are protected with ligands. the perovskite NCs is precipitated with the existence of TiO₂, which involves heterogeneous nucleation on the TiO₂ surface, the tained perovskite NCs show irregular shapes with sub-10 nm size. The morphology and size distribution of 6%CsPbBr₃/TiO₂ and other catalysts are characterized by TEM, as shown in Figure 1(a) Id S1 (SI). Figure S1(a) shows that P25-type TiO₂ (Degussa) possesses a size distribution in the range of 10-50 nm. In Figure a), the CsPbBr₃ NCs can be observed as black dots distributed on the TiO₂ surface. The average size of the monodispersed CsPbBr₃ is 8.3 nm by measuring 50 randomly selected crystals. All CsPbBr₃ NCs are attached on the surface of TiO₂. The density of CsPbBr₃ NCs increases with the CsPbBr₃/TiO₂ mass ratio (Figure S1(b-e)) but without an obvious increase in the size of CsPbBr₃, enabling a ir comparison that screens the size effect towards the photocatalysis. The TEM image of pure CsPbBr₃ nanocrystals is nown in Figure S2 as a comparison.

The lattice of the CsPbBr₃ NCs is further observed by highsolution transmission electron microscopy (HRTEM) as shown in Figure 1(a). Two different lattice fringes, measured from the fast burier transform (FFT) as insets in Figure 1(a), can be found for the 6%CPB/TiO₂ catalyst. The lattice spacing of 0.353 nm can be scribed to the (101) crystallographic plane of the anatase TiO₂ that is the most thermodynamically stable phase.^[30] The lattice g of 0.294 nm corresponds to the (200) plane of CsPbBr₃. They form a physical contact at the interface, which enables an e ficient transfer of photo-generated carriers from CsPbBr₃ to IO₂. The lattice fringes of CsPbBr₃ for other catalysts, e.g. the 11%CPB-Ti as shown in Figure S1(f) with better resolution, which a so agrees with the values calculated from XRD in Figure 1(b).



Figure 1 (a) HRTEM image of 6%CPB/Ti. The CsPbBr₃ and TiO₂ are marked by cycles (dark blue) and squares (light blue). The FFT images with lattice information for TiO₂ and CsPbBr₃ are also displayed in inserts. (b) XRD patterns of 11%CPB/Ti and pure CsPbBr₃, Rutile TiO₂, Anatase TiO₂. (c) EDX elements mapping in the HADDF mode of 6%CPB/Ti.

By comparing the standard XRD patterns of the anatase phase and the rutile phase TiO₂, it can be concluded that the peaks (\Rightarrow) at 20 = 25.3°, 27.1°, 37.8° and 48.0° in Figure 1(b) are characteristic peaks of TiO₂. The P25 TiO₂ employed in this study contains a 75% anatase phase and a 25% rutile phase by integrating the corresponding XRD peaks. The peaks at $2\theta = 15.2^{\circ}$, 21.2°, 30.7°, and 43.8°, correspond to the (001), (110), (002) and (220) planes (*) of CsPbBr₃, respectively, implying the monoclinic phase of the CsPbBr₃ synthesized. When increasing the amount of CsPbBr₃, e.g. 11%CPB/Ti, the diffraction peaks of both TiO₂ and CsPbBr₃ can be observed clearly in the XRD pattern. The HRTEM image indicates that the CsPbBr₃ nanocrystals are strongly attached to the surface of TiO2. The XRD patterns of 4%CPB/Ti, 8%CPB/Ti, 11%CPB/Ti are displayed in Figure S3. The peaks of CsPbBr₃ could barely be observed in 4%CPB/Ti due to the low loading. The XRD patterns, along with the HRTEM, indicate that CsPbBr₃/TiO₂ heterojunction-type catalyst has been successfully obtained using the LARP method.

Besides, the high angle annular dark field (HAADF) image and energy-dispersion X-ray (EDX) mapping images of different elements of 6%CPB/Ti in selected areas (Figure 1c) indicate the overlapping distribution of cesium, lead, and bromine on the TiO_2 surface, and hence confirm the uniform loading of CsPbBr₃ NCs on TiO₂.

Interface interaction and carrier physics

The X-ray photoelectron spectroscopy (XPS) is performed to investigate the interactions between the CsPbBr₃ NCs and TiO₂. The core-level XPS spectra of the Cs, Pb, and Br elements in CsPbBr₃, along with the Ti and O in TiO₂ are measured. The spectra of Cs 3d with binding energy peaks at 738.2 eV and 724.2 eV, Br 3d at 68.2 eV and 69.2 eV in CsPbBr₃, Ti 2p at 464.4 eV and 458.5 eV in TiO₂ for 6%CPB/Ti are shown in Figure S4-S6. The binding energies of the above three elements do not show an obvious shift upon the formation of CsPbBr₃/TiO₂ junction compared with pure CsPbBr₃ and TiO₂. It is worth noting that the Pb 4f peak shows a 0.4 eV shift to the higher binding energy after

loading to TiO₂ compared to the pristine CsPbBr₃ (Figure 2(a)). Meanwhile, the O1s peak in TiO₂ can be deconvoluted into two sub-peaks possibly associating with the Ti-O and Ti-O-H bonding. $^{\left[31\right] }$ Although the binding energy of the Ti-O bond (529.7 eV) remains unchanged, the Ti-O-H bond displays a shift of 0.2 eV (from 531.18 eV to 530.98 eV) to lower binding energy (Figure 2(c)). It suggests the possible chemical interaction between the perovskite and the top surface of TiO₂: 1) the Cs⁺, Br⁻, and Ti⁴⁺ may not be intensively involved in the interaction; 2) the chemical interaction may originate mainly from the coordination between P (II) and the -OH on the TiO₂ surface. The halide vacancy on the surface of perovskite exposes the Pb(II) that may form bonds to the O²⁻ in the -OH on TiO₂, creating the Pb-O-Ti motif and hence anchoring the perovskite NCs on the TiO₂. The bonding between perovskite and TiO₂ may contribute to the improved charge ansfer at the interface.



gure 2 (a) High-resolution XPS spectra of Pb 4f in CsPbBr₃ and 6%CPB/Ti. (b) XPS spectra of O 1s in TiO₂ and 6%CPB/Ti. (c) Enlarged XPS of 1s in OH from Figure. (d) TRPL of CsPbBr₃ and 6%CPB/Ti.

e carrier dynamics is studied by the TRPL spectroscopy. Carrier lifetime indicates the speed of recombination or quenching of photo-generated free electrons/holes or the unseparated ectron-hole pairs (excitons) in the lattice. The TRPL is measured with an excitation laser of wavelength 375 nm. The carrier lifetimes are calculated by fitting the data with the following quation based on a bi-exponential model:

$$y=A_1*exp(-t/\tau_1) + A_2*exp(-t/\tau_2)$$
 (1)

$$\tau_{ave} = (A_1^* \tau_1^2 + A_2^* \tau_2^2) / (A_1^* \tau_1 + A_2^* \tau_2)$$
(2)

wherein the τ_1 represents the attenuation lifetime of excitations in CsPbBr₃ NCs induced by carrier transfer to TiO₂ (for CsPbBr₃/TiO₂ hetero-junction) and the surface recombination on CsPbBr₃ NCs; τ_2 represents the recombination within the bulk of CsPbBr₃; τ_{ave} is the overall average of τ_1 and τ_2 ; A₁, A₂ are the contributing ratio of two different recombination pathway.^[32]

The calculated carrier lifetimes are shown in Table 1 (CsPbBr₃ NCs and 6%CPB/Ti) and S1 (4%CPB/Ti, 8%CPB/Ti, 11%CPB/Ti). Compared with naked CsPbBr₃ NCs, the τ_{ave} of 6%CPB/Ti shows a tremendous decrease from 13.46 to 2.64 ns. Besides, the fast time decay component (τ_1) shows a slight decrease from 1.95 to 1.11 ns upon the contact with TiO₂. This is possibly associated with the PL quenching of CsPbBr₃ by TiO₂ through the electron transfer as a result of the considerable interaction at the interface (also see Figure S7 and Table S1, with data for other comparison catalysts in SI). These data, along with the XPS results, confirm the unique merits of TiO₂ towards the formation of heterojunction with CsPbBr₃ NCs.

 $\label{eq:table_transform} \begin{array}{ll} \textbf{Table 1} & \text{The decay traces and the parameters of the CsPbBr_3/TiO_2} \\ samples. \end{array}$

Sample	τ ₁ (ns)	A1 (%)	τ ₂ (ns)	A2 (%)	τ _{ave} (ns)
CsPbBr ₃ NCs	1.95	78.7	18.06	26.5	13.46
6%CPB/Ti	1.11	77.7	4.09	22.3	2.64

The optical property and photocatalytic performance

The conduction band of TiO₂ (~-4.0 eV vs.Vacuum) is slightly lower than that of CsPbBr₃ (~-3.4 eV vs.Vacuum), which may lead to the formation of the Type II heterojunction.^[33] As shown in Figure 3(a), the ultraviolet-visible (UV-Vis) absorption of pure TiO₂ starts at 420 nm, meaning that the light with a wavelength higher than 420 nm cannot be absorbed. However, the heterojunction structure greatly expands the light absorption range of the catalysts. Upon the loading of perovskite NCs, the light absorption edge is extended from 420 nm to 530 nm. Meanwhile, with the increasing loading of CsPbBr₃, the light absorption within 300-530 nm also dramatically increases (Figure S8), indicating that the CsPbBr₃ NCs serve as the main light absorption material in heterogeneous junction. Figure S9 shows the converted $(\alpha h \upsilon)^2$ - E_g plot where the α is the light absorption coefficient and E_{g} is the photon energy. The absorption edge of the 6%CBP/Ti indicates an optical band gap of 2.32 eV, compared with that of TiO_2 at 3.2 eV.

For the PL measurement, the intensity of the PL peaks represents the radiative recombination process in the materials. For the Type II heterojunction, the photo-induced electrons can be effectively injected into the material with a lower conduction band edge. Hence, the radiative recombination would be suppressed, leading to the reduced PL intensity. Specifically, the photo-excited electrons of CsPbBr₃ NCs will be transferred into TiO₂ that will greatly suppress the radiative recombination and the fluorescence intensity. In Figure 3(b), compared with pristine CsPbBr₃, the PL intensity of 6%CPB/Ti is drastically weakened, suggesting that the photo-excited electrons are efficiently transferred to TiO₂ instead of recombination in the bulk of perovskite NCs (Also in Figure S10). The PL peak of CsPbBr₃ NCs is centered at 518 nm, consistent with the results in the

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literature.^[34] Upon the loading on TiO₂, the peak shows a slight blue shift from 518 nm to 514 nm, probably due to the quantum confinement effect triggered by the different sizes of the pure CsPbBr₃ (50 nm) and the CsPbBr₃ attached on the TiO₂ surface (10 nm).



gure 3 (a) The UV-Vis absorption spectra of TiO_2 and 6%CPB/Ti. (b) The PL spectra of pristine CsPbBr₃ NCs and 6%CPB/Ti. (c) The photocatalytic efficiencies of different catalysts at 60 °C. (d) The photocatalytic efficiencies of 6%CPB/Ti at varied temperatures.

In a short conclusion, with the formation of Type II sterojunction between the CsPbBr₃ NCs and TiO₂, the perovskite NCs can improve the light absorption of TiO₂. The decreasing steady-state fluorescence intensity reflects the efficient separation of photo-generated carrier pairs and the charge transfer by heterojunction structure.

The photocatalytic activities of the catalysts towards the kidation of toluene are evaluated under the visible light irradiation (in a multichannel photochemical reaction device by eijing Perfectlight Technology). A total of 15 mg catalyst is dispersed in 5 mL toluene which is then saturated by O2 and for reactions carried out at 60 °C (see SI for details). Figure 3(c) shows the production rates of benzaldehyde and benzyl a cohol from the oxidation of toluene with different catalysts. The pristine P25 TiO₂ and CsPbBr₃ NCs show much lower catalytic efficiencies than heterojunction structure. Due to the wide h ndgap, the benzaldehyde production rate from TiO₂ is only 653 μ mol g⁻¹h⁻¹. As for the CsPbBr₃ NCs, although they possess a smaller bandgap and more efficient carrier generation, there is a vere problem with the carrier separation due to the quantum confinement and hence the strong radiative recombination. Eventually, the efficiency of the heterojunction-type catalyst is .gher than both components. With the increment of CsPbBr₃, the photocatalytic efficiency first rises and then descends, wherein the highest catalytic efficiency is obtained from the 6%CPB/Ti catalyst. The production rate of benzaldehyde is measured to be 1849 μ mol g⁻¹h⁻¹, almost 3 times that of TiO₂, along with the

production rate of benzyl alcohol at 372 µmol g⁻¹h⁻¹. The selectivity of benzaldehyde of 6%CPB/Ti is calculated to be 82.9%. For the CsPbBr₃ loading less than 6%, the poor light absorption of NCs limits the number of carriers, resulting in lower catalytic efficiency. When the CsPbBr₃ content is higher than 6%, the catalytic efficiency starts to descend again. A possible explanation is that the more DMF used to dissolve the precursors during the synthesis will lead to a higher concentration of polar solvent in the toluene and hence reduce the quality of as-synthesized NCs, resulting in a lower carrier separation efficiency. The product selectivities of the CPB/Ti catalysts are all close to 82% with no significant change, indicating that heterojunction-type catalysts could effectively oxidize toluene to benzaldehyde with high selectivity.

As can be seen from Figure 3(d) (for 6%CPB/Ti), with the elevated reaction temperature, the production rate of benzaldehyde gradually increased from 1089 µmol g⁻¹h⁻¹ at 45 °C to 2356 µmol g⁻¹h⁻¹ at 75 °C, with the production rate of benzyl alcohol also increasing more than 2 times from 205 to 578 µmol g⁻ ¹h⁻¹. The selectivity of benzaldehyde slightly decreases from 84.2% at 45 °C to 80.3% at 75 °C. The 11%CPB/Ti shows a similar temperature dependence with benzaldehyde production rate rising from 620 µmol g⁻¹h⁻¹ at 45 °C to 2026 µmol g⁻¹h⁻¹ at 75 °C (Figure S11). The production rate of benzyl alcohol also rises from 128 to 591 μ mol g⁻¹h⁻¹, within the same temperature span. The selectivity of benzaldehyde decreases from 82.9 % at 45 °C to 77.4% at 75 °C. In summary, with the increase in temperature, the production rates of benzyl alcohol and benzaldehyde also increase. The comparison experiments with 4 other conditions are carried out to confirm the photocatalytic effect of CPB/Ti (Table S2): (a) without O_2 ; (b) without light radiation; (c) without photocatalyst; (d) using only PbBr₂. The results verify that the reactions are catalyzed by the target materials under visible light.

Photocatalytic mechanism

The light-induced electrons and holes are known to possess reduction and oxidation capabilities, respectively. They can capture oxygen and water molecules in the environment and generate superoxide radicals $(\cdot O_2^{-})$ and hydroxyl radicals $(\cdot OH)$, which may both take part in the photocatalytic oxidation reaction. Therefore, 4 different chemicals ammonium oxalate (AO), potassium persulfate (PP), 1, 4-benzoquinone (BQ), and tertbutanol (TPA) are selected as trapping agents to capture the possible photo-generated holes, electrons, $\cdot O_2^{-}$ and $\cdot OH$, respectively.



F ;ure 4 (a) The photocatalytic efficiency of the different trappers. (b) he schematic plot of the heterojunction and the reaction mechanism.

As shown in Figure 4(a), all the catalytic efficiencies reduce after the addition of four sacrificial agents. Upon the addition of A D, the production rate drastically decreases, indicating the articipation of the holes in the rate-limiting step in the whole reaction. For the PP and BQ, they also decrease the production to tes but to a less extent, indicating that the electrons and $\cdot O_2^$ also participate in the photocatalytic reaction. However, as the BA is added, the efficiency only slightly decreases, meaning that the $\cdot OH$ is not involved in the reaction. Based on the above experiments, it can be implied that electrons, holes, and comparison provide free radicals participate in the reaction among which the holes may play a crucial role. Therefore, the reaction achanism is expeculated as follows:

echanism is speculated as follows:

CsPbBr₃/TiO₂+hυ→CsPbBr₃/TiO₂+h⁺+e⁻	(3)
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 $O_2 + e^- \rightarrow O_2^- \tag{4}$

 $C_6H_5CH_3 + h^+ \rightarrow C_6H_5CH_2 + H^+$ (5)

 $C_6H_5CH_2 + O_2 \rightarrow C_6H_5CHO + OH^-$ (6)

 $C_6H_5CH_2 + O_2 \rightarrow C_6H_5CH_2OO$ (7)

 $2C_6H_5CH_2OO \rightarrow C_6H_5CH_2OH + C_6H_5CHO + O_2^{-1}$ (8)

H⁺+ OH⁻→H₂O

 $C_6H_5CH_2OH + h^+ \rightarrow C_6H_5CH_2OH^+$ (10)

 $2C_6H_5CH_2OH^+ + O_2^- \rightarrow 2C_6H_5CHO + H_2O$ (11)

According to the above investigation, a reasonable mechanism fr r the enhanced photocatalytic activity over the CPB/Ti has been proposed. As illustrated in Figure 4(b), the electrons of CsPbBr₃ are excited from the valence band (VB) to the conduction band ('B), producing the photo-generated electron-hole pairs. The electrons transfer from CsPbBr₃ to TiO₂ in the CB with the downhill energy levels at the interface, whereas the holes stay v thin CsPbBr₃. The heterojunction structure could promote the transfer of carriers at the contact interface, hence the photogenerated holes from TiO₂ could easily transfer into CsPbBr₃, and electrons from the CsPbBr₃ can transfer into the CB possibly though the Ti-O-Pb bond. In this way, the formation of \cdot O₂⁻ and R-CH₂· can proceed more efficiently and result in fast photoreaction kinetics from toluene to benzaldehyde.

Conclusions

In summary, the CsPbBr₃/TiO₂ heterojunctions with different ratios are successfully synthesized via the LARP method. Under light illumination, the CsPbBr₃/TiO₂ materials show higher photocatalytic activity for the oxidation of toluene into benzaldehyde than the naked CsPbBr₃ and TiO₂ due to the improved optical absorption and the reduced recombination of photo-generated electron-hole pairs, along with high selectivity. The optimal 6%CPB/Ti sample shows the activity of 2356 µmol g⁻¹h⁻¹ at 75 °C, more than 4 times that of the CsPbBr₃ NCs, and 3 times that of the TiO₂. The XPS result suggests that the Ti-O-Pb coupling at the interface of the two components improves the transport of charge carriers. Furthermore, this study presents a strategy to construct a highly efficient heterojunction-type photocatalytic system based on inorganic halide perovskite materials.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.2018xxxxx.

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