Organic ligands with long carbon chains have been widely utilized to mediate the growth of halide perovskite crystals with tunable morphologies. However, the presence of these surfactants on the surface of halide perovskites limits their performance in photocatalytic conversion applications. Herein, a rapid synthetic protocol to prepare Cs$_3$Bi$_2$Br$_9$ platelets with clean surfaces and controllable thickness in a dilute H$_2$SO$_4$ solution after a quick cooling process in liquid nitrogen or mixtures of dry ice is reported. Electron microscopy and X-ray diffraction reveal the preferential exposure of (00$l$) facets in Cs$_3$Bi$_2$Br$_9$ platelets with variable thickness from 100 to 500 nm. Infrared spectroscopy hints that the selective chemisorption of ethyl acetate on (00$l$) facets of bismuth perovskites regulates the growth of the crystals. These novel lead-free halide perovskite platelets can drive the photo-oxidation of toluene to benzaldehyde with high selectivity ($\geq$88%) and stability over 36 h.

1. Introduction

Among the narrow-bandgap semiconductor materials, all-inorganic halide perovskites (ABX$_3$ with $A$ = Rb, Cs; $B$ = Pb, Sn, Ge; and $X$ = Cl, Br, I) have received growing attention due to their excellent optoelectronic properties, particularly in the case of lead-containing perovskites.\textsuperscript{[1]} With the explosive development in halide perovskite–based solar cells, numerous novel strategies for material synthesis and characterization have emerged to construct perovskite-based optoelectronic devices with higher efficiency and longer lifetime.\textsuperscript{[2]} However, research interest is shifting toward lead-free, stable all-inorganic halide perovskites due to the toxicity of lead, as well as the thermal and moisture instabilities of organic–inorganic hybrid halide perovskites.\textsuperscript{[3]}

Shape-controlled crystals provide appealing chemical and physical properties for diverse applications.\textsuperscript{[4]} To control the morphology and structure of halide perovskites, a ligand-mediated synthesis approach is commonly used.\textsuperscript{[5]} By use of various aliphatic amines or/and acids (e.g., oleylamine and oleic acid) as surfactants in organic solvents such as octadecene, the morphologies can be successfully tuned from 0D dots and 1D rods and wires to 2D platelets, which can be ascribed to the restriction of crystal growth due to strong surface interactions between the halide perovskites and the capping agent.\textsuperscript{[6]} However, ligands with long carbon chains can bind tightly to perovskite surfaces, possibly blocking active sites and resulting in decreases in reaction activity when perovskite nanomaterials are applied as photocatalysts.\textsuperscript{[7]} Clearly, to fabricate efficient halide perovskite–based photocatalysts with clean surfaces, it is essential to develop ligand-free synthetic methods. Although several solution-phase-based protocols exist for producing bulky single crystals or microcrystals without the assistance of surfactants, much of the focus has been on Pb-based perovskites without fine-tuning of the structures.\textsuperscript{[8]}

Notably, halide perovskite microcrystals not only present superior charge transport with ultralong charge carrier diffusion lengths due to low trap density, but also show higher moisture and thermal stability in comparison with polycrystalline counterparts.\textsuperscript{[14b,9]}

Photocatalytic organic transformations, a promising and green synthetic strategy, can be driven by sustainable solar energy under mild conditions.\textsuperscript{[10]} To date, several halide perovskite–based photocatalytic systems have been explored for various visible light–driven organic reactions,\textsuperscript{[11]} such as aldehyde alkylation,\textsuperscript{[12]} alcohol oxidation,\textsuperscript{[13]} thiol coupling,\textsuperscript{[14]} triole conversion,\textsuperscript{[15]} C–C, C–O, and C–N bond formation,\textsuperscript{[16]} polymerization,\textsuperscript{[17]} and dehydrogenation reactions.\textsuperscript{[18]} Very recently, the challenging reaction of direct activation of C(sp$^3$)–H bonds under light irradiation was successfully realized over perovskite photocatalysts (e.g., supported Cs$_3$Bi$_2$Br$_9$ nanoparticles,\textsuperscript{[19]} A$_2$Sb$_2$Br$_9$ nanoparticles,\textsuperscript{[20]} and lead-based NiO$_x$/FAPbBr$_3$/TiO$_2$ perovskite composites).\textsuperscript{[21]} However, the fast degradation of these active perovskite phases severely limits their practical and long-term applications. This mainly originates from the hydrolysis reaction of halide perovskites with water, which is generated during the photo-oxidation of toluene to benzaldehyde.\textsuperscript{[19]} Thus, it is essential to design stable halide perovskites for photocatalytic aerobic oxidation reactions.

Herein, we develop a facile and rapid synthesis method to design lead-free Cs$_3$Bi$_2$Br$_9$ crystals with platelet shapes and variable thickness. In the presence of dilute H$_2$SO$_4$ solution and ethyl acetate (EA) as the directing agent, Cs$_3$Bi$_2$Br$_9$ platelet microcrystals with different thicknesses ranging from 100 to 200 nm were successfully synthesized.
500 nm could be formed after rapid cooling in liquid nitrogen within one minute. When used as active photocatalysts, the Cs$_3$Bi$_2$Br$_9$ platelets can continuously and stably convert toluene to benzaldehyde with a high selectivity (≥88%) after 36 h light irradiation in air.

2. Results and Discussion

The rapid synthetic protocol to prepare Cs$_3$Bi$_2$Br$_9$ halide perovskite crystals is shown in Scheme 1. As bismuth atoms on the perovskite surface serve as Lewis acid sites,$^{[13c]}$ we have used EA as the structure directing agent. This can selectively interact with bismuth atoms via two carbonyl groups to control the crystal growth in an acidic solution. The halide precursors (CsBr and BiBr$_3$) and EA are first dissolved in a dilute H$_2$SO$_4$ solution (13 wt%). Then, the clear acidic solution is placed in liquid nitrogen for a short period (≈1 min) for rapid cooling under rigorous magnetic stirring. Immediately, a yellow suspension is obtained after the rapid cooling. Finally, the fresh Cs$_3$Bi$_2$Br$_9$ crystal sample is produced after centrifuging and washing by isopropanol. Notably, the growth rate of bismuth-based perovskite microcrystals is several orders of magnitude faster than some traditional growth methods for halide perovskite crystals, which can take several days.$^{[22]}$ Moreover, the crystallization rate is comparable with another widely used inverse temperature crystallization method for the preparation of organic–inorganic perovskites, which requires a high thermal treatment temperature in organic solvents.$^{[8a,23]}

The structure and morphology of the materials were characterized using diverse analytical techniques. Based on scanning electron microscopy (SEM) analysis shown in Figure 1a, in the absence of the organic directing agent EA, the halide perovskite Cs$_3$Bi$_2$Br$_9$ crystals are formed with irregular shapes and a wide range of sizes. In contrast, with the addition of EA, Cs$_3$Bi$_2$Br$_9$ platelets can grow with tunable thickness by adjusting the halide perovskite concentrations in the dilute H$_2$SO$_4$ solution (10, 8, 6, and 4 g L$^{-1}$). At a high concentration (10 g L$^{-1}$), large platelet microcrystals with basal plane size up to 40 μm and thickness around 500 nm are produced (Figure 1b and Figure S1a, Supporting Information). Lowering the concentration (8 g L$^{-1}$) reduces the thickness of the platelets to ≈350 nm (Figure S1b, Supporting Information), still resulting in large nonuniform crystals with plane size up to ≈30 μm, as shown in Figure 1c. Because these concentrations (10 and 8 g L$^{-1}$) of perovskite could provide enough salt solutes for the continual growth of crystal nuclei after reaching the supersaturation state, formation of larger and thicker platelets is expected. In contrast, the further decrease of the perovskite concentration to 6 g L$^{-1}$ leads to much smaller platelets (from 10 to 20 μm) with more uniform shape and thickness close to 200 nm (Figure 1d and Figure S1c, Supporting Information). As shown in Figure 1e, when using the lowest concentration of 4 g L$^{-1}$, the thinnest hexagonal platelets with the basal size of 2–10 μm could be obtained and the average thickness decreased to around 100 nm (Figure S1d, Supporting Information).

The surface morphology and elemental composition of the thinnest platelets were further investigated by scanning transmission electron microscopy (STEM). As shown in Figure 1f, the hexagonal platelet crystal displays a smooth surface with plane size of 7 μm even though some smaller fragments of halide perovskite are visible on the surface of the platelet. The elemental mapping of the platelets shows a quite homogeneous distribution of the Cs, Bi, and Br elements in all the regions (Figure 1g–i). Furthermore, as shown in Figure 1j, the quantitative analysis of elemental content based on energy dispersive X-ray spectroscopy (EDX) reveals that the ratio of Cs:Bi:Br corresponds to 3.2:2.0:8.9, which matches well with the theoretical value (Table S1, Supporting Information). In addition, no impurities such as sulfur appear in the spectrum, indicating the pure and clean perovskite composition of the formed Cs$_3$Bi$_2$Br$_9$ platelets.

According to the X-ray diffraction (XRD) measurements (Figure 2), all the Cs$_3$Bi$_2$Br$_9$ microcrystals grown in diluted H$_2$SO$_4$ show the pure perovskite phase with trigonal $P$3$m$1 symmetry and high crystallinity, matching very well with the reference material (PDF#44-0714 card). Without the assistance of EA, the XRD pattern of Cs$_3$Bi$_2$Br$_9$ microcrystals shows no specific growth orientation, which also agrees well with the SEM image (Figure 1a). In contrast, the presence of EA during crystal growth leads to the preferential exposure of (001) facets for all the

Scheme 1. The synthesis procedure for Cs$_3$Bi$_2$Br$_9$ platelet crystals grown in dilute H$_2$SO$_4$ acidic solution with EA as directing agent via rapid cooling down in a liquid nitrogen bath for ≈1 min.
Figure 1. SEM images and elemental analysis of the Cs$_3$Bi$_2$Br$_9$ microcrystals grown in dilute H$_2$SO$_4$. a) SEM image of the irregular crystals grown without the addition of EA. b–e) SEM images of the platelet crystals grown in the presence of EA with different perovskite concentrations of 10, 8, 6, and 4 g L$^{-1}$, respectively. f–i) STEM-based elemental mapping of the thinnest platelets. j) SEM-EDX-based elemental analysis of the thinnest platelets.
Cs$_3$Bi$_2$Br$_9$ platelets, which could be confirmed by the higher intensity diffraction peaks belonging to the (00l) lattice planes. As the larger and thicker platelet samples have preferred crystal orientation, the more intense (00l) diffraction peaks could be observed in the XRD pattern.

To further investigate the influence of the cooling method, we prepared a series of Cs$_3$Bi$_2$Br$_9$ crystals by varying the cooling temperatures at a fixed perovskite precursor concentration of 4 g L$^{-1}$ in the presence of EA. As shown in Figure S2, Supporting Information, when the cooling temperature is increased from $-196$ to $-78$ and $-41$ °C using a mixture of dry ice, acetone, and acetonitrile, similar yellow suspensions appear after a slightly longer time (2 and 3 min, respectively). However, when the temperature rises to $-15$ and 0 °C using dry ice–ethylene glycol and ice–water mixtures as the cooling agent, very small amounts of yellow precipitates are generated. A much longer crystallization time is required (10 and 60 min) to form solid precipitates. In comparison with the hexagonal platelets formed after the rapid cooling at $-196$ °C (Figure S3a,b, Supporting Information), the sample from the cooling temperature of $-78$ °C also exhibits a platelet shape with thickness close to 100 nm and basal plane size in the range 2–8 μm (Figure S3c, d, Supporting Information). In contrast, the higher cooling temperature of $-41$ °C leads to much larger and thicker platelets with the basal size up to 15 μm and thickness of around 200 nm (Figure S3e,f, Supporting Information). Higher cooling temperatures of $-15$ and 0 °C result in quite large and less regular crystals with thickness up to 2 μm (Figure S3g–j, Supporting Information). Overall, a rapid low cooling temperature ($\leq -78$ °C) is essential to generate uniform and thin hexagonal platelets with small basal size. The short crystal growth time prevents further evolution of the basal size of the platelets. In contrast, at a higher cooling temperature ($\geq -15$ °C), the growth and crystallization are much slower. This leads to a lower amount of halide perovskite precipitates with uncontrollable morphologies. Because EA is an effective chelation agent in the sol–gel synthesis of metal oxides (e.g., Al$_2$O$_3$ and TiO$_2$),[24] we can hypothesize that the controllable growth of Cs$_3$Bi$_2$Br$_9$ platelet microcrystals might originate from the interaction between EA and bismuth atoms. The Fourier transform infrared spectroscopy (FT-IR) analysis could indicate this possible interaction between EA and bismuth atoms, as shown in Figure 3a. For the pure EA molecules, the characteristic intense absorption of the ketonic form appears at 1738 and 1713 cm$^{-1}$ because of the stretching modes of two C=O groups (one with a blueshift due to the inductive effect from esteric oxygen). Considering the keto–enol tautomeration, two shoulder bands rise from the C=C in conjunction with a carbonyl group ($\approx$1630 cm$^{-1}$) as well as the hydrogen bonding between C=O and the hydroxyl group ($\approx$1650 cm$^{-1}$). However, when EA is deposited onto the fresh Cs$_3$Bi$_2$Br$_9$ platelets (obtained after washing by isopropanol), the shoulder bands corresponding to the enol tautomer disappear, and new broad IR bands between 1675 and 1500 cm$^{-1}$ emerge in addition to the strong absorption peaks from free EA molecules. These new absorption bands may possibly be

![Figure 2. XRD patterns of the Cs$_3$Bi$_2$Br$_9$ microcrystals grown in dilute H$_2$SO$_4$ in the absence of EA or in the presence of EA with different perovskite concentrations (10, 8, 6, and 4 g L$^{-1}$), including the reference data (PDF#44-0714 card). All the diffraction intensities are normalized based on the (202) diffraction peak.](image-url)

![Figure 3. a) FT-IR analysis of the fresh thinnest Cs$_3$Bi$_2$Br$_9$ platelets and their deposition with EA, including pure EA as reference. b) Steady-state PL spectra of the Cs$_3$Bi$_2$Br$_9$ platelets synthesized with different perovskite concentrations (10, 8, 6, and 4 g L$^{-1}$).](image-url)
from the C—O vibration in the enolate bonded to bismuth and C—C vibration of the six-membered complex ring.[23] Similar but much more intense and well-resolved absorption bands appear in the cases of strong Lewis acid metals (Al or Ti) chelated with EA.[24a,24c,26] Importantly, the obtained fresh Cs$_3$Bi$_2$Br$_9$ platelets show clean surfaces after simple washing with alcoholic solvents such as isopropanol. This is clearly evidenced by the FT-IR spectrum where all the characteristic bands related to EA have vanished (Figure 3a). Thus, chemisorbed EA molecules could be easily washed away because of the weak Lewis acidity of bismuth.[13c] Moreover, to further study the key role of the carbonyl groups in EA during the synthesis of Cs$_3$Bi$_2$Br$_9$ platelets, EA is replaced by another organic additive (ethyl acetate) that only contains one carbonyl group. Even though the as-prepared Cs$_3$Bi$_2$Br$_9$ crystals still exhibit a platelet shape, the thickness varies in quite a broad range from 300 nm to 1 μm with very large basal plane size of up to 20 μm (Figure S4, Supporting Information). This morphology variation could be associated with weaker interactions between ethyl acetate and bismuth sites in contrast to the EA. Thus, it can be hypothesized that the organic directing agent (e.g., with multiple carbonyl groups) interacting more strongly with bismuth atoms results in better control of the crystal growth of Cs$_3$Bi$_2$Br$_9$.

The optical properties of Cs$_3$Bi$_2$Br$_9$ platelet crystals were investigated by UV–vis diffuse reflectance (UV–vis DRS) and steady-state photoluminescence (PL) spectroscopy. All of the Cs$_3$Bi$_2$Br$_9$ platelets prepared from different perovskite concentrations display visible light absorption with the same optical bandgap of 2.64 eV (Figure S5, Supporting Information). Furthermore, a broad PL emission peak (from 450 to 550 nm) centered at 480 nm is seen in all Cs$_3$Bi$_2$Br$_9$ platelets with different thicknesses (Figure 3b). The rising intensity below 450 nm is from the excitation light at 400 nm. The broad PL emission band could reflect multiple defect states with different energy levels, which may come from the cracked surfaces of large platelet crystals.[27] The emission intensity gradually decreases when the platelets become larger and thicker, suggesting the suppressed radiative recombination of electron–hole pairs on more bulky crystals with less trap states. Instead, the Cs$_3$Bi$_2$Br$_9$ nanoparticles (size from 50 to 500 nm) exhibit an intense PL emission peak with a blue-shift at 475 nm in contrast to the platelet microcrystals (Figure S6, Supporting Information), indicating superior charge separation in Cs$_3$Bi$_2$Br$_9$ microcrystals with low trap densities.[22]

As proof of concept for the direct activation of C(sp$^3$)—H bonds using solar light, the photo-oxidation of toluene was explored as the model reaction using the thinnest Cs$_3$Bi$_2$Br$_9$ platelets as photocatalysts. The Cs$_3$Bi$_2$Br$_9$ platelets show twofold higher photocatalytic activity in contrast to the bulkier crystals with irregular shapes grown in the absence of EA (Figure S7, Supporting Information). This could be attributed to the enhanced crystallinity and crystal orientation of the thin Cs$_3$Bi$_2$Br$_9$ platelets, which can facilitate charge extraction and transfer.[28] The thickness of the large platelets has a very limited effect on the selective photo-oxidation of toluene (Figure S8, Supporting Information) as all the platelet samples possess high crystallinity and good charge transport ability.

In Figure 4a, the time-dependent photocatalytic reaction clearly demonstrates the high activity and long-term stability of the platelet perovskite photocatalyst, which converts 232 μmol of toluene in total after 36 h light irradiation in air. The corresponding benzaldehyde yield reaches 2.2% with 9.4 mmol net toluene as reactant (Table S2, Supporting Information). Moreover, a high selectivity (≥88%) toward benzaldehyde was achieved and benzyl alcohol was produced as the main byproduct, while less than 3% of benzoic acid was detected as well. The conversion rate increases with the irradiation time during the first 8 h (starting from 2.5 μmol h$^{-1}$) and stays relatively stable for another 28 h (7.3 μmol h$^{-1}$). In contrast, the supported Cs$_3$Bi$_2$Br$_9$ nanoparticles became totally deactivated after a short reaction time of 8 h, where the photocatalyst changes to white in color because of the complete hydrolysis of the bismuth halide perovskite to the BiOBr phase.[19] Herein, the robust Cs$_3$Bi$_2$Br$_9$ platelet microcrystals maintain their yellow color for 24 h (Figure S9, Supporting Information), implying the high resistance and stability of the materials. The sample after 36 h irradiation shows a pale yellow color (Figure S9, Supporting Information). In addition, UV–vis DRS analysis of the used photocatalyst after 36 h irradiation shows a similar optical bandgap (2.65 eV) in comparison with the fresh sample (2.64 eV), even
though the absorption bands in the UV region change from the double peak to the single one (Figure S10, Supporting Information). This minor change may indicate some variation in the surface chemical environment of the Cs\textsubscript{3}Bi\textsubscript{2}Br\textsubscript{9} platelets, possibly involving surface hydroxylation due to water attack that is produced from the catalytic reaction as a side product. The postreaction SEM characterization clearly shows that most of the hexagonal platelets with lateral size in the micrometer range (2–10 μm) are turned into smaller particles after long-term irradiation (Figure S11c,d, Supporting Information). This morphology transition may come from the continuous grinding of the magnetic stirring bar and the cracking due to the attack of water molecules.[290] The surfaces of the hexagonal platelet crystals appear to be quite rough and with plenty of cracks after the photocatalytic reaction of 36 h.

To further understand the mechanism for photo-oxidation of toluene, a series of control experiments was conducted in the presence of different scavengers, as shown in Figure 4b. First, no catalytic reaction took place in the absence of light or photocatalysts, demonstrating the photocatalytic nature of toluene oxidation under solar light irradiation over Cs\textsubscript{3}Bi\textsubscript{2}Br\textsubscript{9} platelets. The addition of isopropanol (IPA) as hole scavenger dramatically suppresses the photo-oxidation of toluene. Meanwhile, butylated hydroxytoluene (BHT), a carbon-centered radical trap, can prohibit the reaction completely. In contrast, a sacrificial electron acceptor (CCl\textsubscript{3}) leads to only a slight activity loss. Furthermore, the presence of tert-butanol (TBA) shows negligible influence, suggesting no participation from hydroxyl radicals. Regarding the role of reactive oxygen species (ROS), the addition of Tiron (disodium 4,5-dihydroxy-1,3-benzenedisulfonate-4,5-dihydroxy-1,3-benzenedisulfonate) as superoxide scavenger induced only a small deceleration of photocatalytic toluene oxidation. This hints that ROS are not directly involved in the rate-determining step of C(O)H cleavage. The coupling product of 1,2-diphenylethane was detected when the reaction was conducted in Ar (Figure S12, Supporting Information), although almost no oxygenated products were formed. This clearly demonstrates that holes at the valence band maximum (VBM) are essential for the C–H bond activation.

It should be noted that the VBM level of Cs\textsubscript{3}Bi\textsubscript{2}Br\textsubscript{9} is close to 2.17 eV (vs SHE) based on our previous study,[19] which is not more positive than the oxidation potential of toluene (=2.2 V vs SHE).[130] However, the oxidation of toluene by VBM holes can lead to the generation of benzyl radicals with H\textsuperscript{+} species transferred to the catalyst surface (excited surface-Br\textsuperscript{•−} [h\textsuperscript{+}] + PhCH\textsubscript{3} → PhCH\textsubscript{2}• + surface-Br •− H\textsuperscript{+}). This can be regarded as a concerted proton–electron transfer step (CPET).[186] This is similar to the NO\textsubscript{3}• radical-driven oxidation mechanism, which is another typical example of a CPET process.[184] Therefore, photoexcited holes play a crucial role in the activation of C(sp\textsuperscript{2})–H bonds at the methyl group of toluene, which is consistent with reported cases.[19,26]

3. Conclusion

In conclusion, herein a practical rapid protocol is developed to prepare Cs\textsubscript{3}Bi\textsubscript{2}Br\textsubscript{9} halide perovskite crystals with controllable morphologies. Using EA as the structure-directing agent, a series of pure Cs\textsubscript{3}Bi\textsubscript{2}Br\textsubscript{9} platelets with tunable thickness (from 100 to 500 nm) has been successfully prepared in a dilute H\textsubscript{2}SO\textsubscript{4} acidic solution. The EA allows controllable growth of lead-free bismuth halide perovskite platelets with clean surfaces and preferential exposure of (001) facets after rapid cooling in liquid nitrogen and dry ice mixtures. All Cs\textsubscript{3}Bi\textsubscript{2}Br\textsubscript{9} platelet microcrystals show reduced radiative charge recombination and visible light absorption. Moreover, the Cs\textsubscript{3}Bi\textsubscript{2}Br\textsubscript{9} platelets shows satisfactory catalytic performance for photo-oxidation of toluene to valuable benzaldehyde with high selectivity (≥88%) and stability, lasting for 36 h without obvious deactivation. This simple and ultrafast crystal growth approach in acidic aqueous media could be potentially used to prepare a range of halide perovskite crystals for diverse applications, including optoelectronic device manufacturing and photocatalysis fields.

4. Experimental Section

Raw Materials: The following commercial reagents were used directly from Sigma-Aldrich: BiBr\textsubscript{3} (purity ≥98%), CsBr (99.9% trace metals basis), DMSO (purity ≥99%), IPA (ACS reagent, ≥99.5%), acetone (ACS reagent, ≥99.5%), EA (ReagentPlus, 99%), H\textsubscript{2}SO\textsubscript{4} (ACS reagent, 95.0-98.0%), toluene (ACS reagent, ≥99.5%) and trifluorotoluene (anhydrous, ≥99%).

Cs\textsubscript{3}Bi\textsubscript{2}Br\textsubscript{9} Preparation: To prepare the Cs\textsubscript{3}Bi\textsubscript{2}Br\textsubscript{9} platelets, first various quantities of perovskite precursors CsBr and BiBr\textsubscript{3} (corresponding to the Cs\textsubscript{3}Bi\textsubscript{2}Br\textsubscript{9} concentration of 10, 8, 6, and 4 g L\textsuperscript{−1}) were dissolved in 25 mL diluted H\textsubscript{2}SO\textsubscript{4} acid (13 wt%). Meanwhile, 1 mL EA as the organic directing agent was added to the acidic solution (1 mL acetone was added together to assist the total dissolution of EA). To study the role of carbonyl groups in the structure-directing agent on the morphology control of the platelets, 1 mL ethyl acetate (contains only one carbonyl group) was added to replace EA for comparison. Subsequently, the acidic aqueous solution was placed in a liquid nitrogen bath with vigorous magnetic stirring for a short period of time of around 1 min. Immediately, a yellow suspension was generated, which was then centrifuged and washed by isopropanol. Finally, yellow Cs\textsubscript{3}Bi\textsubscript{2}Br\textsubscript{9} platelets were obtained after drying in a vacuum oven at 50 °C for 12 h. In comparison, Cs\textsubscript{3}Bi\textsubscript{2}Br\textsubscript{9} microcrystals with irregular shapes were prepared with the perovskite concentration of 10 g L\textsuperscript{−1} in the absence of EA. Furthermore, in the case of 4 g L\textsuperscript{−1} perovskite precursor concentration, different cooling methods were tested to investigate the temperature influence. Specifically, the mixtures of dry ice–acetone, dry ice–acetoneitrile, dry ice–ethylene glycol, and ice–water were used as cooling agents to reach temperatures of −78, −41, −15, and 0 °C, respectively.

 Characterization: SEM/SEM-EDX were performed using a tabletop microscope (Hitachi TM3030Plus) equipped with a primary secondary electron detector at an accelerating voltage of 15 keV. The integrated EDX spectrometer (AZtec Series from Oxford Instruments, UK) has a silicon drift detector (SDD) with a detection area of 30 mm\textsuperscript{2}. STEM-based elemental mapping tests were recorded on a Hitachi S-5500 In-lens field emission scanning electron microscope at 30 kV with an EDX SDD (Thermo Scientific UltraDry). XRD data were collected in reflection mode using an STOE θ/θ diffractometer with Bragg–Brentano geometry (Cu K\textalpha radiation). FT-IR profiles were collected on a Spectrum Two FT-IR spectrometer (PerkinElmer) in the attenuated total reflection (ATR) mode. UV–vis DRS spectra were obtained by the use of a PerkinElmer Lambda 365 UV–vis spectrophotometer equipped with an integrating sphere. BaSO\textsubscript{4} (spectroscopy grade) was used as a reference and all the measurements were performed with a wavelength range from 300 to 800 nm. PL spectra were recorded on an Edinburgh FSS spectrofluorometer with 2.5 mg sample dispersed in 10 mL IPA and the excitation wavelength was 400 nm.

Photocatalytic Evaluation: The photocatalyst (5 mg) was added to 10 mL pure toluene with 0.2 mmol trifluorotoluene as internal standard to obtain a yellow suspension in a home-made steel autoclave (25 mL), which was
sealed with a borosilicate window to enable the top illumination. Then, the autoclave with reaction suspension was placed in a cooling jacket (293 K) and excited with a 300 W Xenon-arc lamp in 1 bar air atmosphere. After irradiation, the liquid phase was quantitatively measured using gas chromatography (GC) or gas chromatography–mass spectrometry (GC–MS) with trifluorotoluene as the internal standard. For the control tests, various scavenger reagents (CCl₄, isopropanol, Tiron, BHT and TBA) were added with the molar amount of 0.3 mmol.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

Research data are not shared.

**Keywords**

bismuth halide perovskites, Cs₅Bi₃Br₁₀ platelets, photocatalytic C–H bond activation, solar energy conversion

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[1] a) M. V. Kovalenko, L. Protesescu, M. I. Bodnarchuk, L. Protesescu, M. I. Bodnarchuk, M. V. Kovalenko, L. Protesescu, M. I. Bodnarchuk, Adv. Sci. 2020, 8, 28824; d) A. Chakrabarty, S. Satija, U. Gangwar, S. Sapra, Chem. Mater. 2020, 32, 721.
[2] a) J. Shamsi, A. S. Urban, M. Imran, L. De Trizio, L. Manna, Chem. Rev. 2019, 119, 3296; b) G. Almeida, L. Goldoni, Q. Akkerman, Z. Dang, A. H. Khan, S. Marras, I. Moreels, L. Manna, ACS Nano 2018, 12, 1704.
[3] a) A. Pan, B. He, X. Fan, Z. Liu, J. J. Urban, A. P. Alivisatos, L. He, Y. Liu, ACS Nano 2016, 10, 7943; b) S. Sun, D. Yuan, Y. Xu, A. Wang, Z. Deng, ACS Nano 2016, 10, 3648; c) D. Amgar, A. Stern, D. Rotem, D. Porath, L. Egar, Nano Lett. 2017, 17, 1007.
[4] a) M. I. Saidaminov, A. A. Abdelhady, B. Murali, E. Alarousu, V. M. Burlakov, W. Peng, I. Dursun, L. Wang, Y. He, G. Maculan, A. Goriely, T. Wu, O. F. Mohammed, O. M. Bakr, Nat. Commun. 2015, 6, 7586; b) Q. Liao, K. Hu, H. Zhang, X. Wang, J. Yao, H. Fu, Adv. Mater. 2015, 27, 3405; c) Q. Dong, Y. Fang, Y. Shao, P. Mulligan, J. Qiu, L. Cao, J. Huang, Science 2015, 347, 967; d) Z. Zhu, W. Deng, W. Li, F. Chun, C. Luo, M. Xie, B. Pu, N. Lin, B. Gao, W. Yang, Adv. Mater. Interfaces 2021, 8, 2000182.
[5] a) D. Shi, V. Adinolfi, R. Comin, M. Yuan, E. Alarousu, A. Buin, Y. Chen, S. Hoogland, A. Rothenberger, K. Katsiev, Y. Losovoy, X. Zhang, P. A. Dowben, O. F. Mohammed, H. E. Sargent, O. M. Bakr, Science 2015, 347, 519; b) Y. Song, W. Bi, A. Wang, X. Liu, Y. Kang, Q. Dong, Nat. Commun. 2020, 11, 274.
[6] L. Marzo, S. K. Pagire, O. Reiser, B. König, Angew. Chem., Int. Ed. 2018, 57, 10034.
[7] a) H. Huang, B. Pradhan, J. Hofkens, M. B. J. Roelfaers, J. A. Steele, ACS Energy Lett. 2020, 5, 1107; b) Y. Lin, J. Guo, J. San Martin, C. Han, R. Martinez, Y. Yan, Chem. Eur. J. 2020, 26, 13118; c) C. Yuan, Y. He, R. Chen, Y. Sun, J. Li, W. Cui, P. Chen, J. Sheng, F. Dong, Sol. RRL 2021, 5, 2000419.
[8] X. Zhu, Y. Lin, Y. Sun, M. C. Beard, Y. Yan, J. Am. Chem. Soc. 2019, 141, 733.
[9] a) H. Huang, H. Yuan, K. P. F. Janssen, G. Solís-Fernández, Y. Wang, C. Y. X. Tan, D. Jonckheere, E. Debroye, J. Long, J. Hendrix, J. Hofkens, J. A. Steele, M. B. J. Roelfaers, ACS Energy Lett. 2018, 3, 755; b) S. Schüemann, M. van Gastel, H. Tüysüz, ChemSusChem 2018, 11, 2057; c) M. Zhang, Z. Li, X. Xin, J. Zhang, Y. Feng, H. Lv, ACS Catal. 2020, 10, 14973.
[10] W.-B. Wu, Y.-C. Wong, Z.-K. Tan, J. Wu, Catal. Sci. Technol. 2018, 8, 4257.
[11] a) W. Deng, K. Li, W. Luo, C. Zhu, H. Guan, H. Wang, K. Deng, H. Zhou, X. Ye, B. Yi, L. Li, Q. Chen, Angew. Chem., Int. Ed. 2020, 59, 12931.
[12] X. Zhu, Y. Lin, J. San Martin, Y. Sun, D. Zhu, Y. Yan, Nat. Commun. 2019, 10, 2843.
[13] a) H. Chen, X. Deng, G. Dodekatos, H. Tüysüz, J. Am. Chem. Soc. 2017, 139, 12267.
[14] a) X. Zhu, Y. Chen, H. Yuan, K. F. Janssen, G. Solís-Fernández, Y. Wang, C. Y. X. Tan, D. Jonckheere, E. Debroye, J. Long, J. Hendrix, J. Hofkens, J. A. Steele, M. B. J. Roelfaers, ACS Energy Lett. 2018, 3, 755; b) S. Schüemann, M. van Gastel, H. Tüysüz, ChemSusChem 2018, 11, 2057; c) M. Zhang, Z. Li, X. Xin, J. Zhang, Y. Feng, H. Lv, ACS Catal. 2020, 10, 14973.
[15] d) A. Wang, X. Mao, S. Yang, Y. Li, Y. Wang, M. Wang, W. Deng, K. Han, ACS Appl. Mater. Interfaces 2020, 12, 2100265.
1998, 8, 1241; c) Kurajica, I. Škorić, I. Lozić, V. Mandić, Mater. Chem. Phys. 2014, 147, 1058; d) H. B. Tran, L. T. T. Pham, Y. Lee, H. B. Jang, S. Kim, I. Kim, J. Catal. 2019, 372, 86.

[25] S. Kurajica, Chem. Biochem. Eng. Q. 2019, 33, 295.

[26] S. Kurajica, G. Mali, T. Gazivoda, J. Sipusic, V. Mandić, J. Sol-Gel Sci. Technol. 2009, 50, 58.

[27] P. Wu, J. Wang, J. Zhao, L. Guo, F. E. Osterloh, J. Mater. Chem. A 2014, 2, 20338.

[28] Y. Dai, Q. Bu, R. Sooriyagoda, P. Tavadze, O. Pavlic, T. Lim, Y. Shen, A. Mamakhel, X. Wang, Y. Li, H. Niemantsverdriet, B. B. Iversen, F. Besenbacher, T. Xie, J. P. Lewis, A. D. Bristow, N. Lock, R. Su, J. Phys. Chem. Lett. 2019, 10, 5381.

[29] M. Leng, Y. Yang, K. Zeng, Z. Chen, Z. Tan, S. Li, J. Li, B. Xu, D. Li, M. P. Hatzinger, Y. Fu, T. Zhai, L. Xu, G. Niu, S. Jin, J. Tang, Adv. Funct. Mater. 2018, 28, 1704446.

[30] K. Gardner, J. Mayer, Science 1995, 269, 1849.

[31] a) R. Tomat, A. Rigo, J. Appl. Electrochem. 1986, 16, 8; b) D. R. Weinberg, C. J. Gagliardi, J. F. Hull, C. F. Murphy, C. A. Kent, B. C. Westlake, A. Paul, D. H. Ess, D. G. McCafferty, T. J. Meyer, Chem. Rev. 2012, 112, 4016.