High-efficiency visible-light-driven oxidation of primary C–H bonds in toluene over CsPbBr₃ perovskite supported by hierarchical TiO₂ nanoflakes†

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Photocatalytic oxidation of toluene to valuable fine chemicals is of great significance, yet challenged in the development of advanced catalysts with both high activity and selectivity for the activation of inert $C(sp^3)$–H bonds. Halide perovskites with remarkable optoelectronic properties have shown to be prospective photoactive materials, but the bulky structure with small surface area and severe recombination of photogenerated electron-hole pairs are obstacles to application. Here, we fabricate a hierarchical nanoflower-shaped CsPbBr₃/TiO₂ heterojunction by assembling CsPbBr₃ nanoparticles on 2D TiO₂ nanoflakes subunits. The design significantly downsizes the size of CsPbBr₃ from micrometer to nanometer, and forms type II heterojunction with intimate interfacial contact between the CsPbBr₃ and the TiO₂ nanoflakes, thereby accelerating the separation and transfer of photogenerated charges. Moreover, the formed hierarchical heterojunction heightens light absorption by the refraction and scattering, offers large surface area and enhances the adsorption of toluene molecules. Consequently, the optimized CsPbBr₃/TiO₂ exhibits a high performance (10200 µmol g^{-1} h^{-1}) for photocatalytic toluene oxidation with high selectivity (85%) for benzaldehyde generation under visible light. The photoactivity is about 20 times higher than blank CsPbBr3, and is among the best photocatalytic performance reported for selective oxidation of toluene under visible light irradiation.

Introduction

The direct oxidation of toluene to high-added-value fine chemicals, such as alcohols and aldehydes, is one of the most important conversions in chemical industry.[1-4] However, due to the inertness and high bond dissociation energy (89.8 kcal mol^{-1}) of the $C(sp^3)$–H bond,[5] the activation of toluene generally need to be operated under harsh reaction conditions (high pressure and temperature) and with the assistance of specific metal complexes or aggressive oxidants, which is expensive, energy intensive and causes negative impacts on the environment.[6-8] Solar-driven photocatalytic aerobic oxidation using molecular O₂ as oxidant represents a promising methodology to overcome these challenges, but the overall photocatalytic performance reported so far is still unsatisfactory due to the lack of desired photocatalysts with broad optical absorption windows, efficient charge separation, and high product selectivity.[9-11]

Over the past years, halide perovskite materials have triggered wide attention in photocatalysis because of their outstanding optical and electronic properties.[12-16] The high charge carrier mobility, visible light absorption, and tunable band structures enable them to be potential competitors for photocatalytic oxidation of toluene.[17,18] Nevertheless, single-component halide perovskites typically evolve to bulky aggregates with large particle size (several to tens micrometers), which leads to severe bulk recombination of charge carriers and restricts the photoactivity.[19,20] To tackle the problem, construction of heterojunction is an effective strategy. By hybridization of the halide perovskite with preferred substrates, it not only can prevent the aggregation of the halide perovskites to mediate the bulk recombination of photoexcited electron–hole pairs, but also can establish interfacial built-in electric field to further facilitate the spatial charge transfer and separation.[21]

Moreover, the catalytic functions of photocatalysts also strongly depend on the nanostructure.[22,23] To realize high photocatalytic performance, the delicate design of well-defined nanostructure for heterojunction composites is also critical.[24-27] For diverse structural configurations, 3D hierarchical flower-like nanostructure constructed by 2D nanoflakes subunits have demonstrated intrinsic advantages for photocatalysis. Such hierarchical structure can strengthen the light absorption of photocatalysts by multi-light reflection and scattering within the nanoflakes subunits, and prohibit the aggregation of the 2D nanoflakes to afford large surface area with abundant active sites.[28,29] In addition, the nanoflakes subunits will greatly shorten the diffusion path of charges, thereby facilitating the separation and transfer of photogenerated charges to surface for redox reactions.[30,31] Thus, the development of advanced 2D subunits-assembled hierarchical structure with heterogeneous junction would be promising for high-efficiency photocatalytic toluene oxidation.

Here, inspired by these above considerations, we design and fabricate a hierarchical nanoflower-shaped CsPbBr₃/TiO₂

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(abbreviated as CPB/TiO$_2$) heterojunction composed of TiO$_2$ nanoflakes-supported all-inorganic CsPbBr$_3$ perovskite nanoparticles. Benefiting from the composition and nanostructure engineering, the CPB/TiO$_2$ heterojunction displays excellent performance for photocatalytic toluene oxidation under the irradiation of visible light. The optimized 20%CPB/TiO$_2$ heterojunction composite delivers a toluene conversion rate of 10200 µmol g^{-1} h^{-1} and a high selectivity of 85% towards benzaldehyde (benzyl alcohol as the main by-product). The performance outperforms most of the state-of-the-art catalysts in literature for visible-light-driven oxidation of toluene. This work provides a new idea by constructing hierarchical heterojunction structure over halide perovskite materials for high-efficiency photocatalytic toluene conversion.

Experimental section

Materials

Cesium bromide (CsBr, 99.999%), lead bromide (PbBr$_2$, 99.0%) and tetrahydrofuran (THF), were purchased from Macklin (Shanghai, China). N, N-Dimethylformamide (DMF), toluene, tetrabutyl titanate (TBOT), ethanol (EtOH), concentrated hydrochloric acid (HCl, 36%), acetic acid and glycerol were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals and solvents were used without further purification.

Synthesis of mesoporous hierarchical TiO$_2$ nanoflowers

Typically, 1.5 g of Pluronic F127 was dispersed into a mixed solvent of 2.4 mL acetic acid, 3.2 mL concentrated hydrochloric acid (HCl) and 30 mL tetrahydrofuran (THF). After vigorously stirring for 20 min, 3.4 mL tetrabutyl titanate (TBOT) and 0.2 mL H$_2$O were added subsequently to obtain a clear primrose yellow solution. After that, the solution was dried in an oven at 45 °C for 24 h to form a light-yellow gel. Then, 1.0 g of the gel was added into 25 mL ethanol (EtOH) and 5 mL glycerin under vigorous stirring. After 20 min, the transparent solution was transferred to a 50 mL Teflon-lined autoclave, heated at 150 °C for 15 h, and then cooled naturally to room temperature. The precipitation was washed with ethanol, and dried at 60 °C in oven.[32] Finally, the precipitation was calcinated in a Muffle furnace at 400 °C for 5 h with a heating rate of 1 °C min^{-1} to obtain the hierarchical TiO$_2$ nanoflowers. To synthesize the collapsed TiO$_2$ without hierarchical nanoflower structure, the precipitation was calcinated in the same Muffle furnace at 400 °C for 5 h, but with a heating rate of 5 °C min^{-1}.

Synthesis of CsPbBr$_3$/TiO$_2$ composites and blank CsPbBr$_3$

CsPbBr$_3$/TiO$_2$ composites were synthesized according to an antisolvent precipitation method at room temperature.[33] Typically, 1 mmol CsBr and 1 mmol PbBr$_2$ were dissolved in 10 mL of N, N-Dimethylformamide (DMF) by ultrasonication to form a precursor solution. Meanwhile, 100 mg TiO$_2$ was dispersed into 10 mL of DMF and stirred to form a uniform white dispersion. Then a certain amount of the CsPbBr$_3$ precursor solution was added into the TiO$_2$ dispersion under ultrasonication. Then, the mixture was added dropwise into 50 ml toluene and stirred vigorously for 30 min. After that, the solution was centrifuged at 8000 rpm for 3 min. The precipitation was collected and dried in a vacuum oven. The series of x% CsPbBr$_3$/TiO$_2$ composites were synthesized by changing the volume of the added CsPbBr$_3$ precursor solution, where x is the mass ratio of CsPbBr$_3$ in the composite (x = 10, 20, 30, 40). Blank CsPbBr$_3$ was prepared by the same procedure without the addition of TiO$_2$.

Characterizations

Scanning electron microscopy (SEM) images were captured by Hitachi 8100. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were recorded using a JEM-2100F EX microscope at an accelerating voltage of 200 kV. The Brunauer-Emmett-Teller (BET) specific surface area was measured by N$_2$ adsorption-desorption instrument (BELSORP-mini II). The X-ray diffraction (XRD) patterns of the catalysts were characterized on a Bruker D8 advance X-ray diffractometer operated at 40 kV and 40 mA with a Cu Kα radiation in the 2θ ranging from 10° to 80°. The UV-Vis diffuse reflectance spectra (DRS) were obtained on a CARY-100 spectrophotometer (Agilent) using 100% BaSO$_4$ powder as a standard sample. X-ray photoelectron spectroscopy (XPS) was recorded by an X-ray photoelectron spectrometer (Thermo Escalab 250 electron spectrometer) with Al-Ka radiation. Raman spectra were obtained using a laser at a wavelength of 785 nm (Thermo Fisher Scientific, DXR 2xi). Photoluminescence (PL) spectra of solid samples were obtained by an RF-5301PC spectrophotometer (Shimadzu, Japan) with the 435 nm excitation wavelength.

Electron paramagnetic resonance (EPR) measurements were performed at room temperature using a Magnettech ESR5000X spectrometer. In general, 10 mg samples were dispersed in a mixed solution of 2 mL CH$_3$CN containing 1 mL toluene and 2 µL 5,5-dimethyl-1-pyrroline-N-oxide (DMPO). The suspension was then transferred into a glass capillary. The sealed glass tube was then placed in the microwave cavity of the EPR spectrometer and exposed to a 300 W Xe lamp source (CEL-PF300-T8, Beijing China Education Au-light Co., Ltd.) at room temperature.

Photoelectrochemical measurements

The photoelectrochemical analysis was carried out in a conventional three-electrode cell using a Pt plate and an Ag/AgCl electrode as the counter electrode and the reference electrode, respectively. The working electrode was prepared on fluorine-doped tin oxide (FTO) glass that was cleaned by ultrasonication in ethanol for 1 h. Typically, 5 mg of the catalyst was dispersed in 0.5 mL of isopropanol to get a slurry. After that, 20 µL of the slurry was dropped onto FTO with a size of 1 cm^2 and dried in air. The electrochemical impedance spectroscopy (EIS) measurement was performed in an electrolyte of tetrabutylammonium hexafluorophosphate (TBAPF$_6$) in ethyl acetate (EA). Transient photocurrent was tested in the same electrolyte and A 300 W Xe lamp (CEL-PF300-T8, Beijing China

Education Au-light Co., Ltd.) equipped with a 420 nm cutoff filter ($\lambda \geq 420$ nm) is used as light source. Mott-schottky measurement was performed in an electrolyte of 0.1 M TBAPF$_6$ in CH$_2$Cl$_2$.

Density functional theory (DFT) calculations

DFT calculations were carried out using the Vienna ab initio simulation package (VASP) with the projector-augmented-wave (PAW) method.[34] The Perdew-Burke-Ernzerhof (PBE) scheme was used for the exchange correlation function, employing the generalized gradient approximation (GGA).[35] The electronic wave function was expanded using a plane wave basis with an energy cutoff of 500 eV. The energy convergence criterion was set to 1.0×10^{-5} eV, and the force convergence criterion was set to 0.03 eV Å^{-1} for each atom. For the CsPbBr$_3$ (110) and TiO$_2$ (101) slabs, a $6 \times 3 \times 1$ and $3 \times 9 \times 1$ k-point mesh was used, respectively. A 30 Å vacuum layer along the z direction was adopted to prevent unintended periodic interactions between adjacent slabs. The CsPbBr$_3$/TiO$_2$ heterostructure model consists two CsPbBr$_3$ layers and one TiO$_2$ layer, with a 20 Å vacuum space along the z direction. To saving computing resources, a $1 \times 1 \times 1$ k-point mesh was employed for CsPbBr$_3$/TiO$_2$ heterostructure. The van der Waals interactions between TiO$_2$ and CsPbBr$_3$ were taken into account using the DFT-D3 correction method.

Photocatalytic activity measurements

All photocatalytic reactions were conducted in a quartz reactor. Typically, 10 mg photocatalyst and 1 mL toluene (9.4 mmol) were dispersed in a reactor containing 2 mL acetonitrile. The reactor was purged with O$_2$ for 10 min, and then irradiated by visible light ($\lambda > 420$ nm) with a 300 W Xe lamp (CEL-PF300-T8, Beijing China Education Au-light Co., Ltd.). After light irradiation of 2 h, the liquid product was analyzed by a gas chromatography (GC-2030, Shimadzu, Japan, FID detector, nitrogen (N$_2$) as carrier gas) after centrifuging the suspension at 10000 rpm for 3 min.

Results and discussion

Characterizations of catalysts

The 3D hierarchical CPB/TiO$_2$ heterostructure was prepared by a simple anti-solvent precipitation method with the addition of TiO$_2$ nanoflowers into the precursor solution of CsPbBr$_3$, as schematically illustrated in **Fig. 1a**. X-ray diffraction (XRD) was exploited to characterize the crystal structure of the blank CsPbBr$_3$, CPB/TiO$_2$ composites and TiO$_2$. As shown in **Fig. 1b**, the diffraction peaks at 15.1°, 21.5°, 30.7°, 34.4°, and 43.8° can be ascribed to monoclinic CsPbBr$_3$ (100), (110), (200), (210) and (220) planes (JCPDS No. 18-0364).[36-38] In addition, the peaks at 25.3°, 37.7°, 48.0°, 53.8°, 55.0°, 62.6° can be attributed to the (101), (004), (200), (105), (211), and (204) planes of anatase TiO$_2$, respectively.[32] The XRD patterns of CPB/TiO$_2$ composites indicate both characteristic peaks of CsPbBr$_3$ and TiO$_2$, and the peaks intensity of the CsPbBr$_3$ increases as the CsPbBr$_3$ content increasing (**Fig. S1†**).
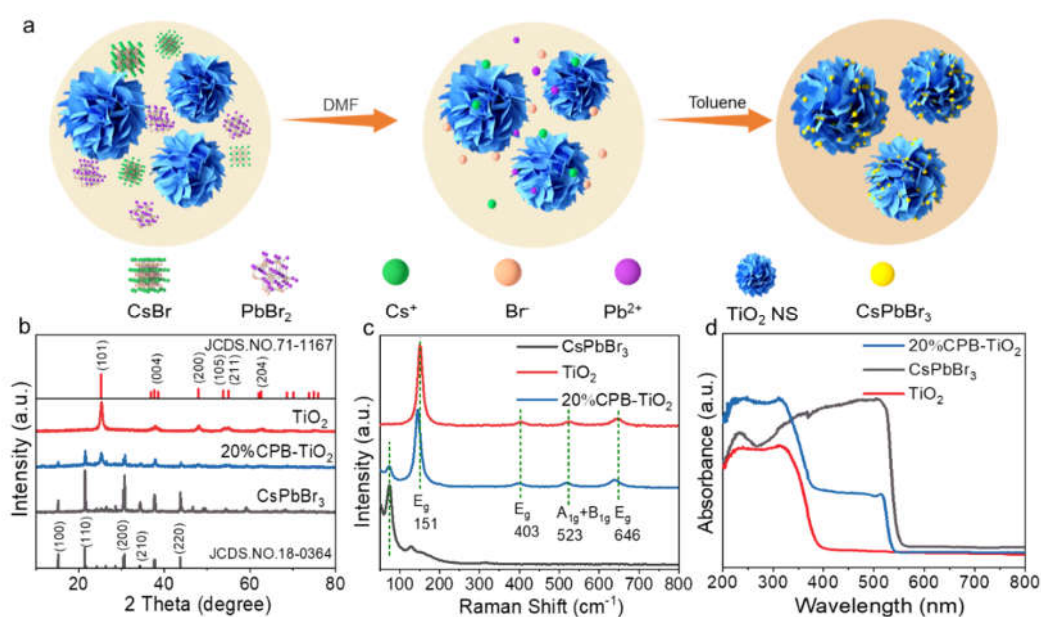
Fig. 1. (a) Schematic diagram for the synthesis of 3D nanoflower-shaped CPB/TiO$_2$ heterostructure. (b) XRD patterns, (c) Raman spectra, and (d) UV-Vis DRS spectra of CsPbBr$_3$, CPB/TiO$_2$ and TiO$_2$.

Raman spectra was used to further confirm the composition of the synthesized catalysts. As shown in **Fig. 1c**, the peaks at 151 cm^{-1} (E$_g$), 403 cm^{-1} (E$_g$), 523 cm^{-1} (A$_{1g}$+B$_{1g}$), and 646 cm^{-1} (E$_g$) belong to the anatase TiO$_2$ vibration modes. A new peak of 74 cm^{-1} assigned to the vibrational mode of [PbBr$_6$]$^{4-}$ octahedron of CsPbBr$_3$ is observed in the CPB/TiO$_2$.[39-41] The characteristic peak of CsPbBr$_3$ is also enhanced with the increment of the loading amount of CsPbBr$_3$ (**Fig. S2†**). This coincides with the XRD analysis, validating the successful preparation of the CPB/TiO$_2$ composites. Notably, after the growth of CsPbBr$_3$ on the TiO$_2$ nanosheets, the Raman peaks of TiO$_2$ shift to a lower wavenumber compared to that of blank TiO$_2$. The shift indicates an increasing of bond length and decreasing of the bond energy of the Ti−O bond, which can be attributed to the strong electrostatic interaction between the CsPbBr$_3$ and the TiO$_2$.[42-45] **Fig. 1d** shows the UV–vis diffuse reflectance spectroscopy (DRS) analysis of the samples, which is employed to assess the optical absorption properties. It can be seen that the light absorption edge of blank TiO$_2$ is around 390 nm, denoting its UV light response nature. After integrating with CsPbBr$_3$, the light absorption of CPB/TiO$_2$ is extended to approximately 540 nm. Meantime, the absorption edge of TiO$_2$ at 390 nm can also be detected. This should be ascribed to the hybridization of high weight content of CsPbBr$_3$ with TiO$_2$ support. As such, both absorption features are present in the composite. The greatly extended light absorption enables the visible-light-excitation of the CPB/TiO$_2$ composites to be possible, which is beneficial for promoting the solar energy utilization. With the increase of CsPbBr$_3$ content, the visible light absorption of CPB/TiO$_2$ is also gradually enhanced (**Fig. S3†**). Moreover, in comparison with blank CsPbBr$_3$, it is notable that the visible light absorption edge of the hybrid CPB/TiO$_2$ composite is slightly blue shifted (*ca.* 14 nm). This can be attributed to the quantum size effect resulted from the smaller size of CsPbBr$_3$ in the composite. The inference has been demonstrated by the following scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analyses.
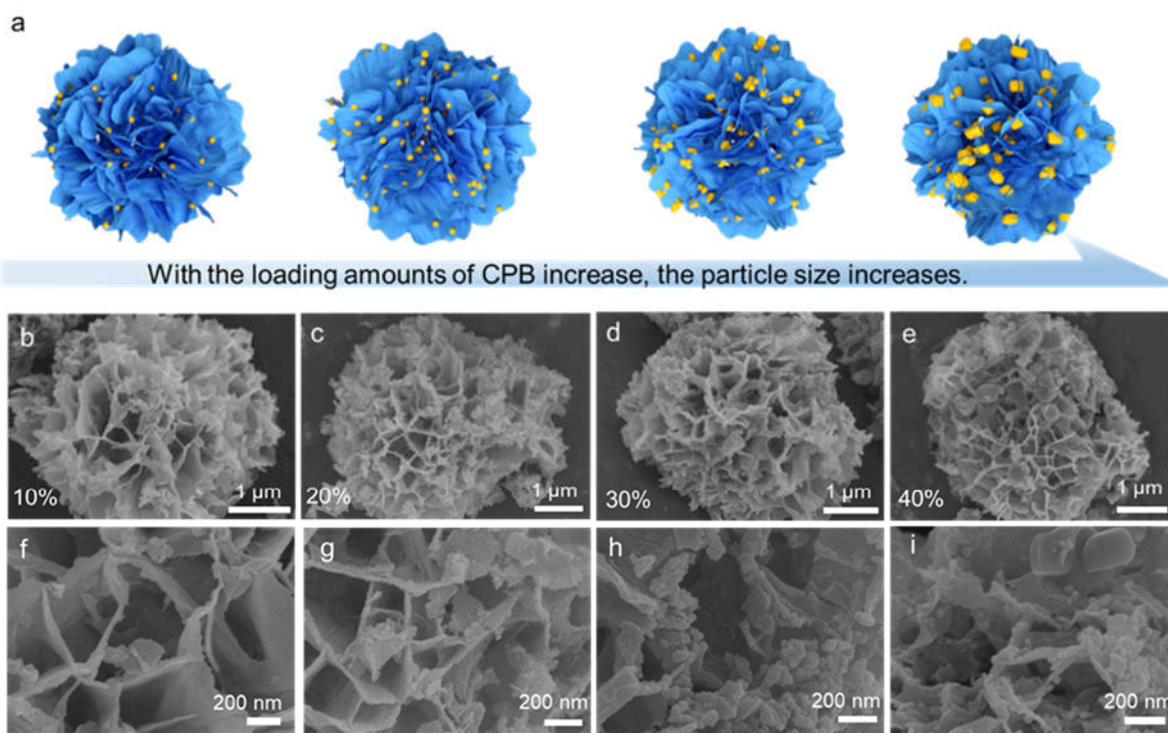
Fig. 2. (a) Schematic and (b-i) SEM images showing the morphology evolution of x% CPB/TiO$_2$ (x = 10, 20, 30, 40) composites.

As shown in **Fig. 2** and **Fig. S4-S5†**, SEM is firstly utilized to characterize the morphology and microstructure of the CPB/TiO$_2$, blank TiO$_2$ and CsPbBr$_3$ samples. The blank TiO$_2$ presents a nanoflower shape, which is assembled by vertical nanoflakes (**Fig. S4†**). The surface of the nanoflakes subunits is clean and smooth. For blank CsPbBr$_3$, it shows a large particle morphology and the particle sizes range from 0.9 to 2.0 μm (**Fig. S5†**). After the construction of the CPB/TiO$_2$ heterojunction, the TiO$_2$ nanoflower-shaped structure is maintained (**Fig. 2**), while the surface of the nanoflakes subunits becomes rough due to the in-situ growth of CsPbBr$_3$. From **Fig. 2b-2i**, it can be clearly seen that for all the CPB/TiO$_2$ samples, the sizes of the CsPbBr$_3$ particles in the composites are much smaller than that of blank CsPbBr$_3$, indicating that the formation of heterojunction is beneficial for preventing the aggregation and reducing the size of the CsPbBr$_3$ halide perovskite. This can be ascribed to that

the presence of TiO_2 nanoflower with nanoflakes subunits can act as heterogeneous nuclei site to facilitate the nucleation and growth of the $CsPbBr_3$, which generates more seeds and leads to the smaller size of the $CsPbBr_3$ particles.[20] The significantly decreased particle size could greatly promote the exposure of surface active sites and inhibit the charge recombination of $CsPbBr_3$ under light irradiation. Moreover, it is notable that with the increase of the $CsPbBr_3$ contents from 10% to 40% in the composites, the particle sizes of $CsPbBr_3$ are increased, as schematically illustrated in **Fig. 2a**. This can be attributed to the further growth of $CsPbBr_3$ at high concentrations.

To further obtain the microscopic structure information of the samples, transmission electron microscopy (TEM) analysis is carried out. Taking the $20\%CPB/TiO_2$ as an example, the TEM image of the sample (**Fig. 3a** and **b**) shows a nanoflakes structure of TiO_2. The surface is rough and densely covered by small $CsPbBr_3$ nanoparticles. Since that the sample for TEM analysis is prepared by strong ultrasonication, the well-defined $CsPbBr_3$ nanoparticles on the 2D nanoflakes surface indicates intimate interfacial contact between the two components. Meanwhile, the intensive coverage of $CsPbBr_3$ forms large contact interface with TiO_2 nanoflakes, which is conducive to

the migration of charge carriers across the CPB/TiO_2 heterojunction.[46] Moreover, nanopores can be observed on the CPB/TiO_2, which is resulted from the mesoporous structure of the TiO_2 nanoflakes, as demonstrated by the N_2 adsorption-desorption analysis (**Fig. S6†**). High-resolution TEM (HRTEM) image (**Fig. 3c**) shows distinct lattice fringe of 0.35 nm and 0.41 nm, corresponding to the (101) planes and (110) planes of anatase TiO_2 and monoclinic $CsPbBr_3$, respectively. Furthermore, **Fig. 3d** shows the corresponding energy dispersive X-ray spectroscopy (EDS) elemental mappings analysis of the $20\%CPB/TiO_2$. Cs, Pb, Br, Ti and O elements are uniformly distributed on the nanoflakes structure, indicating that $CsPbBr_3$ and TiO_2 are well combined. The results further verify the formation of CPB/TiO_2 hybrid composite with intimate interfacial contact. Moreover, in comparison with blank TiO_2, the $20\%CPB/TiO_2$ composite displays smaller specific surface area (**Table S1†**), which can be attributed to that the growth of $CsPbBr_3$ nanoparticles on the surface of TiO_2 may aggregate in the TiO_2 pores. Correspondingly, the total pore volume of $20\%CPB/TiO_2$ is also slightly lower than that of blank TiO_2. The result matches with the SEM measurement.
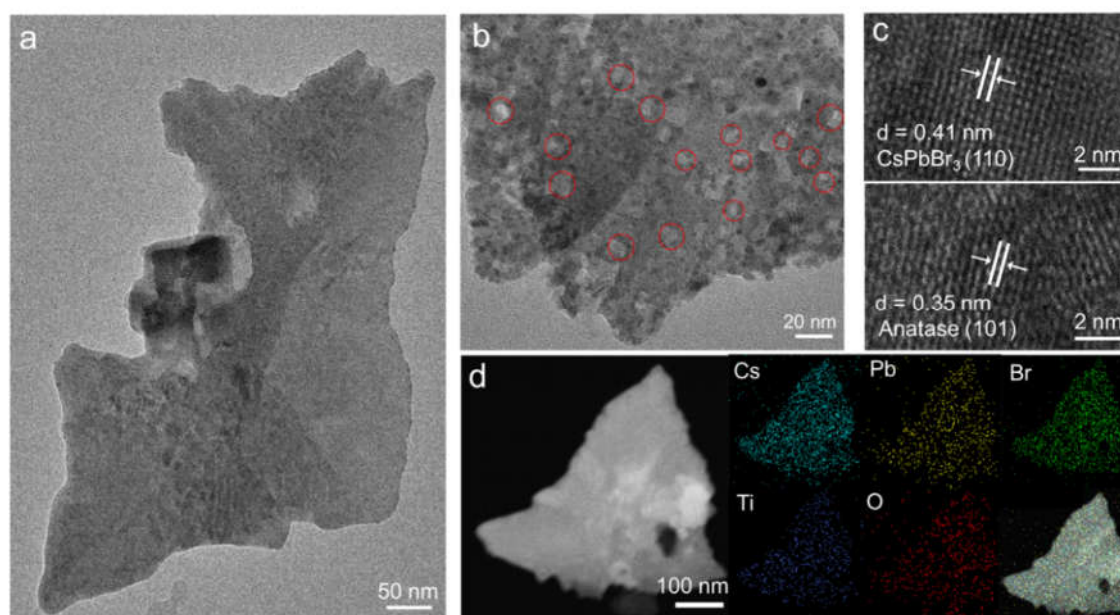

Fig. 3. (a, b) TEM images, (c) HRTEM image, and (d) corresponding EDS elemental mapping images of $20\%CPB/TiO_2$.

To study the surface chemical states of the samples, X-ray photoelectron spectroscopy (XPS) has been performed. As shown in **Fig. 4a**, the presence of Cs, Pb, Br, O and Ti elements can be detected from the XPS survey spectrum of CPB/TiO_2. The high-resolution spectrum of Ti 2p shows two peaks of Ti $2p_{3/2}$ and Ti $2p_{1/2}$ at 458.5 eV and 464.2 eV (**Fig. 4b**), which indicates that Ti element mainly exists as Ti^{4+} ions. For the O 1s pattern (**Fig. 4c**), it can be divided into two peaks, which are attributed to the lattice O (Ti−O) and hydroxyl O (−OH). **Fig. S7†** shows the fine-scanned Cs 3d XPS spectrum, the two peaks with binding energies at 724.2 eV and 738.1 eV are assigned to Cs $3d_{5/2}$ and

Cs $3d_{3/2}$, indicating that the chemical state of the Cs in the composite is +1. The Pb 4f spectrum in **Fig. 4d** shows characteristic peaks at 138.0 eV and 142.9 eV, corresponding to Pb $4f_{7/2}$ and Pb $4f_{5/2}$ orbitals of Pb^{2+} ion. Moreover, the Br 3d is decomposed into two peaks at 67.9eV and 68.9 eV, corresponding to the binding energies of Br $3d_{5/2}$ and $3d_{3/2}$, attributed to the presence of Br^- (**Fig. 4e**). It is worth noting that for the CPB/TiO_2 composite, the Ti 2p and O 1s peaks show a negative shift of 0.2 eV in comparison with blank TiO_2 (**Fig. 4b** and **c**). In contrast, the binding energies of Cs 4d, Pb 4f, and Br 3d in the CPB/TiO_2 show a positive shift (**Fig. 4d-e and S7†**),

which are higher than those of blank $CsPbBr_3$ by 0.4 eV. The results verify the strongly interacted interface with electron transfer from the $CsPbBr_3$ to the TiO_2 nanosheets in the heterostructure, which is in accordance with the Raman analysis. To further clarify the interaction and electron transfer at the interface, density functional theory (DFT) calculation has been carried out. **Fig. 4g** and **h** shows the work functions of the TiO_2 (101) and $CsPbBr_3$ (110) slabs, which are 7.09 eV and 4.63 eV, respectively, corresponding to the Fermi levels (E_f) of -3.61 eV and -2.51 eV (vs. the vacuum level). Due to the lower E_f value

of TiO_2 than that of blank $CsPbBr_3$, the electrons would be migrated from the $CsPbBr_3$ to the TiO_2 at the heterojunction interface until their E_f are aligned. Similar result is obtained from the calculated planar-averaged charge density difference of CPB/TiO_2. As shown in **Fig. 4f**, the light cyan and yellow regions indicate the charge depletion and accumulation area, respectively. The calculation results reveal that the cyan region is mainly on the $CsPbBr_3$ side, while the yellow region is on the TiO_2 side, further validating the transfer of electrons from $CsPbBr_3$ to TiO_2. This is consistent with the XPS analysis results.
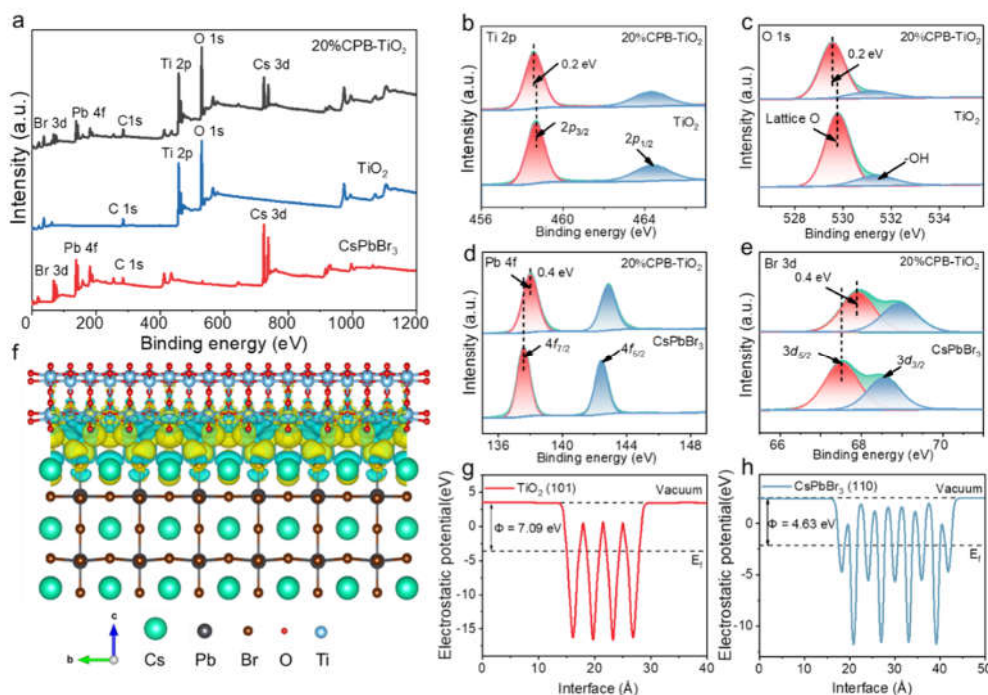
Fig. 4. XPS spectra of $CsPbBr_3$, TiO_2 and 20%CPB/TiO_2: (a) survey, (b) Ti 2p, (c) O 1s, (d) Pb 4f and (e) Br 3d. (f) Charge density differences in the CPB/TiO_2 composite. (g, h) The work functions of blank TiO_2 and $CsPbBr_3$.

Photocatalytic performances

Collectively, the above characterizations faithfully verify the successful fabrication of CPB/TiO_2 hybrid composites with intimate interfacial contact and strong chemical interaction. The presence of TiO_2 nanoflower with 2D nanoflakes subunits greatly inhibits the agglomeration of the halide perovskites, while the $CsPbBr_3$ extends the light absorption range of TiO_2. In view of the desired structural and optical properties, the photocatalytic oxidation of toluene over the hybrid CPB/TiO_2 composites has been tested. A 300 W Xeon lamp equipped with a 420 nm cutoff filter is utilized as a visible light source. It is well known that the solvent/reactant ratio has great influence on the oxidation of toluene,[2,47] thus, the reaction condition of different acetonitrile/toluene ratio is firstly optimized using the 20%CPB/TiO_2 as an example. As shown in **Fig. 5a**, as the ratio of toluene increases from 0.3 to 1 mL, the photoactivity of the 20%CPB/TiO_2 composite gradually increases. The catalyst shows the highest toluene conversion rate of 10200 μmol g^{-1} h^{-1} when

the volume ratio of acetonitrile solvent and toluene reactant is 2:1. The enhanced photoactivity can be attributed to that the increased toluene concentration enhances the reaction possibility between the photogenerated charge carriers and the toluene molecules. However, further increase of the toluene to 1.5 mL and 2 mL decreases the conversion rate. This might be ascribed to the excess adsorption of toluene reactant on the catalyst surface, which would slow down the desorption of the BA and BAD products and suppress the oxidation activity.[48] Based on the result, the following photoactivity tests of all the other samples are carried out under the optimized condition with the acetonitrile/toluene ratio of 2:1.

Fig. 5b shows the visible-light-driven photocatalytic performances of the blank $CsPbBr_3$ and the CPB/TiO_2 composites with different ratios of CPB for the selective oxidation of toluene. The blank $CsPbBr_3$ exhibits a low activity with generation rates of 390 μmol g^{-1} h^{-1} for BAD and 130 μmol g^{-1} h^{-1} for BA. The unsatisfactory photocatalytic performance should be due to the severe charge recombination caused by

the large particle size of CsPbBr₃. For blank TiO₂, it presents no activity. This is reasonable since that the TiO₂ has no visible light absorption and cannot be excited by visible light. In contrast, after the hybridization of CsPbBr₃ with TiO₂, the photocatalytic performances of all the hierarchical CPB/TiO₂ heterojunctions are significantly improved. The best photocatalytic toluene oxidation activity is achieved over the 20%CPB/TiO₂ composite, which shows a toluene conversion rate of 10200 μmol g^{-1} h^{-1} (BAD production rate of 8670 μmol g^{-1} h^{-1} and BA generation rate of 1530 μmol g^{-1} h^{-1}). The photoactivity is about 20 times higher than blank CsPbBr₃, which is also among the top photocatalytic performance reported so far for UV and visible-light-driven selective oxidation of toluene (**Fig. 5c** and **Table S2 †**). The apparent quantum efficiency (AQE) of the 20%CsPbBr₃/TiO₂ composite reaches 2.9% at λ = 420 nm for the

transformation of toluene into BA and BAD (**Fig. S14†**). The gas chromatography-mass (GC-MS) analysis of the reaction solution after light irradiation reveals four peaks, which are ascribed to acetonitrile solvent, toluene reactant, BAD and BA products (**Fig. S8†**). No other product or intermediate is detected, validating the high selectivity of the reaction. With the increase of CsPbBr₃ loading to higher contests (30% and 40%), it results in a performance degradation. This may be ascribed to that: (1) an excess of halide perovskite tends to aggregate into large particles, which will lead to longer migration distances of charge carriers and increase charge recombination; (2) the coverage of excessive and oversized CsPbBr₃ on TiO₂ surface will lead to the reduction of the exposed surface area, inhibiting the adsorption of toluene molecules.
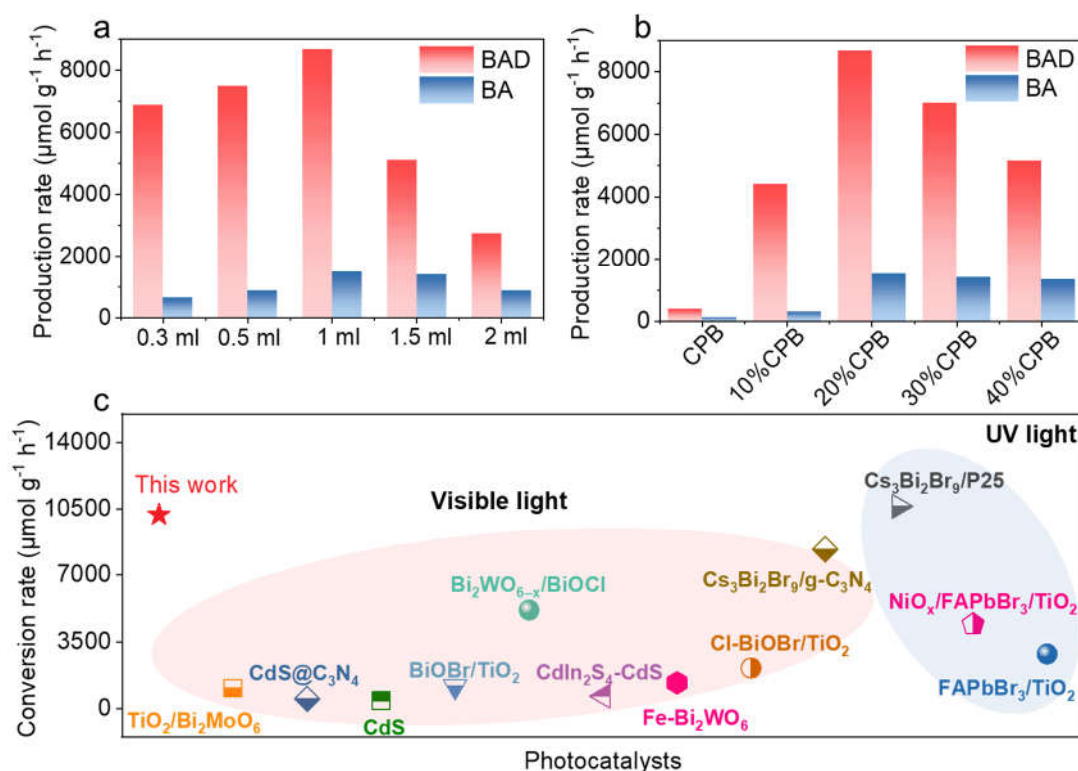

Fig. 5. (a) Photocatalytic oxidation of toluene with different toluene amount in acetonitrile solvent over 20%CPB/TiO₂. The total volume is 3 ml. (b) Photocatalytic oxidation of toluene over blank TiO₂, CPB/TiO₂ composite and blank CsPbBr₃. (c) Performance comparison with reported photocatalysts for UV and visible-light-driven selective oxidation of toluene.

Furthermore, the broad applicability of the CPB/TiO₂ photocatalyst is investigated for photocatalytic selective oxidation of C(sp³)–H of toluene derivatives with different substituents. As shown in **Table 1**, these aromatics are efficiently converted into corresponding aldehydes and alcohols. The selectivity for the aldehyde product is higher than 70%. Notably, the substrate with electron-withdrawing substituents (-F, -Cl, -Br) displays lower photocatalytic activity. This can be attributed to that the electron-withdrawing groups on benzene ring inhibit the abstraction of hydrogen from the methyl group. [49] [50] In addition, p-xylene shows a higher toluene conversion rate (12746 μmol g^{-1} h^{-1}) than its isomers of o-xylene (9900 μmol

g^{-1} h^{-1}) and m-xylene (10930 μmol g^{-1} h^{-1}), which can be attributed to the steric hindrance of the methyl groups hindering the reactant adsorption and activation on the catalyst surface.[51,52]

Moreover, the cycle test of the 20%CsPbBr₃/TiO₂ has been carried out. After repeating the photoactivity test for 4 cycles (**Fig. S16†**), the catalyst still maintains a high activity with negligible decrease in the conversion rate of toluene. In addition, the used 20%CsPbBr₃/TiO₂ has been further characterized by XRD and XPS (**Fig. S17†–S18†**). No obvious change in the crystal structure and surface chemical state is

observed for the composite before and after reaction. These results validate the high stability of the CsPbBr₃/TiO₂ composite.

Photoelectric properties

In order to better understand the reasons for the improved photocatalytic performance, the band structures of the CsPbBr₃ and the TiO₂ are investigated by Mott-Schottky (M-S) measurement and DRS analysis. As shown in **Fig. 6a** and **b**, the positive slopes indicate that CsPbBr₃ and TiO₂ are typical n-type semiconductors.[53] The flat band potential (E_{FB}) are calculated to be -0.86 V and -0.34 V (vs. NHE) for CsPbBr₃ and TiO₂, respectively. Usually, the conduction band potential (E_{CB}) for n-type semiconductor is more negative of about 0.1 eV than E_{FB}.[54] Thus, the E_{CB} of CsPbBr₃ and TiO₂ are concluded to -0.96 V and -0.44 V (vs. NHE), respectively. In addition, the corresponding bandgaps of TiO₂ and CsPbBr₃ are estimated by Tauc plots transformed from the DRS spectra (**Fig. S9†**), which are 3.20 eV and 2.28 eV, respectively. Based on these, the valance band positions (E_{VB}) of CsPbBr₃ and TiO₂ can be calculated as 1.32 V and 2.76 V. As a result, a type-II heterojunction is formed between the CsPbBr₃ and the TiO₂ because of the staggered band structures.

Table 1. Photocatalytic oxidation of C(sp³)–H in substituted toluene over 20%CPB/TiO₂.[a]

Entry	Substrates	Conversion rate ($\mu mol\ g^{-1}\ h^{-1}$)	Selectivity (%)	
			A	B
1		10200	85	15
2		5950	83	17
3		9040	88	12
4		9770	87	13
5		9900	76	24
6		10930	72	28
7		12746	71	29

[a] Reaction conditions: catalyst (10 mg 20%CPB/TiO₂), substrate (1 mL), MeCN (2 mL),1 atm of O₂, 2 h irradiation with visible light (λ > 420 nm).

To study the influence of the heterojunction structure on the transfer behavior of photogenerated charge carriers, transient photocurrent and electrochemical impedance spectra (EIS) tests are performed. As shown in **Fig. 6c**, under visible light irradiation, both CsPbBr₃ and CPB/TiO₂ show rapid and stable photocurrent responses, while TiO₂ does not. This can be attributed to the inability of TiO₂ to be excited by visible light (**Fig. 1d**). In addition, the photocurrent intensity of blank CsPbBr₃ is markedly lower than that of 20% CPB/TiO₂. This should be due to the agglomerated large particle size of the blank CsPbBr₃, which leads to a severe recombination of photogenerated charge carriers.[54] Moreover, **Fig. 6d** shows the Nyquist plots of the samples, which is employed to investigate the interfacial charge transfer efficiency.[55] In general, the smaller diameter of the semicircular arc in the Nyquist plots reflects the lower electron transfer resistance. It can be found that the 20%CPB/TiO₂ sample has the minimum arc radius, which means the best electronic conductivity and charge separation ability.[56,57] Furthermore, the steady-state photoluminescence (PL) spectra are also used to examine the charge separation efficiency. As shown in **Fig. S19†**, the 20%CsPbBr₃/TiO₂ composite shows a much lower PL intensity than CsPbBr₃, revealing that the charge recombination is significantly suppressed in the composite. In addition, the TiO₂ shows no obvious PL signal. This is in accordance with the photocurrent analysis that the TiO₂ is unable to be excited to generate charge carriers by visible light. These photoelectrochemical findings highlight that the construction of the type-II heterojunction between CsPbBr₃ and TiO₂ could effectively accelerate charge transfer, thus contributing to improving the photocatalytic performance.
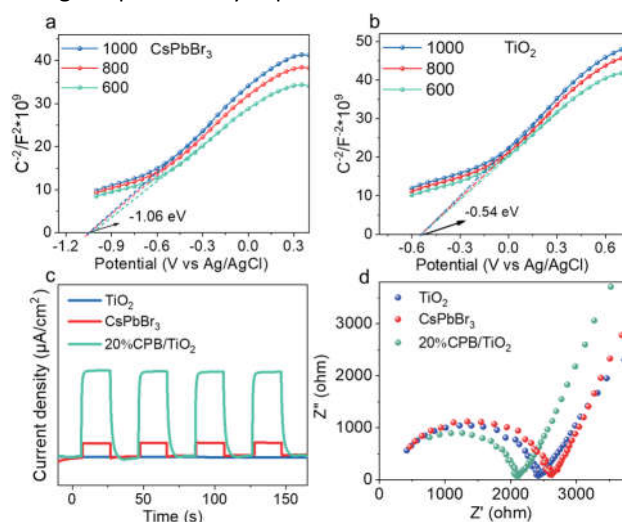

Fig. 6. (a, b) M-S plots of CsPbBr₃ and TiO₂. (c) Transient photocurrent responses, and (d) EIS Nyquist plots of blank TiO₂, CsPbBr₃ and CPB/TiO₂ composite.

Furthermore, for heterogeneous photocatalytic reactions, the effective adsorption of reactant on the catalyst surface is another requisite for the ignition of the redox reaction.[23, 58-60] The BET surface area and porous structure analyses of the TiO₂, CsPbBr₃ and 20%CPB/TiO₂ samples have shown that the

introduction of TiO_2 nanoflower significantly improves the specific surface area and pore volume of 20%CPB/TiO_2 in comparison with that of blank TiO_2 (**Fig. S6†** and **Table S1†**). Generally, larger specific surface area and porous structure enables better adsorption capacity, and exposure of more active sites of catalysts. To further reveal the contribution of the heterostructure for the reactant adsorption, Fourier transform infrared (FTIR) spectroscopy is used to identify the adsorbed toluene species on the $CsPbBr_3$, TiO_2 and 20%CPB/TiO_2 surface. As shown in **Fig. 7a**, for all the three samples after adsorption equilibrium, the typical absorption peaks of toluene are observed, including the C–H stretching vibration of the aromatic ring at 3083 and 3038 cm^{-1}, the skeleton vibration of aromatic ring at 1606 and 1495 cm^{-1}, and the C–H symmetric and asymmetric stretching of methylene group at 2934 and 2875 cm^{-1}.[61-62] Notably, the signal of toluene molecules of 20%CPB/TiO_2 is obviously higher than that of blank $CsPbBr_3$, yet is lower than blank TiO_2. The result indicates that the introduction of TiO_2 can promote the toluene adsorption capacity of CPB/TiO_2, which is conducive to the catalytic conversion.
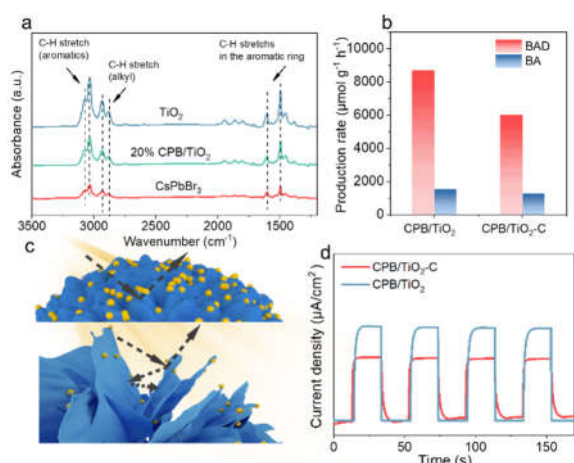
Fig. 7. (a) FTIR spectra of 20%CPB/TiO_2, TiO_2 and $CsPbBr_3$ after adsorption of saturated toluene. (b) Photoactivity comparison between CPB/TiO_2 and CPB/TiO_2-C. (c) Schematic diagram of light absorption over CPB/TiO_2 and CPB/TiO_2-C. (d) Transient photocurrent responses of CPB/TiO_2 and CPB/TiO_2-C.

Finally, to investigate the influence of the hierarchical flower-like nanostructure constructed by 2D nanoflakes subunits on the photocatalytic performance, a collapsed 20%CPB/TiO_2 catalyst (marked as 20%CPB/TiO_2-C) without such structure has been fabricated for comparison. As shown in **Fig. 7b**, the photoactivity test reveals that the 20%CPB/TiO_2-C has a BAD generation rate of 6000 $\mu mol\ g^{-1}\ h^{-1}$ and a BA production rate of 1250 $\mu mol\ g^{-1}\ h^{-1}$, which is notably lower than the CPB/TiO_2. **Fig. S10†** shows the morphology analysis of the 20%CPB/TiO_2-C, which reveals a bulky grain structure with a rough surface. $CsPbBr_3$ nanoparticles are dispersed on the surface of the massive TiO_2. The size of the $CsPbBr_3$ particles in the composite is also much smaller than that of blank $CsPbBr_3$, which once again proves that TiO_2 plays a critical role in inhibiting the growth of $CsPbBr_3$. Nevertheless, compared with 20%CPB/TiO_2,

the size of the $CsPbBr_3$ particles is much larger in the 20%CPB/TiO_2-C. The result validates that the TiO_2 nanoflakes are more beneficial in preventing the agglomeration of the $CsPbBr_3$ particles.

In addition, UV-vis DRS is performed to study the optical absorption property of the 20%CPB/TiO_2-C. The sample shows a similar absorption edge as that of 20%CPB/TiO_2, but the light absorption intensity in the range of 200-550 nm is lower (**Fig. S11†**). The result indicates that the 3D hierarchical CPB/TiO_2 structure is more efficient for solar energy collection, which can be attributed to the multiple light reflection and refraction caused by the vertical nanoflakes, as schematically illustrated in **Fig. 7c**. Meanwhile, the transient photocurrent response test displays that the 20%CPB/TiO_2 exhibits a higher photocurrent density than that of CPB/TiO_2-C under visible light irradiation, indicating more efficient charge transfer (**Fig. 7d**). This can be related to the fact that TiO_2 nanoflakes facilitates the formation of smaller $CsPbBr_3$ particle, which could shorten the charge transfer distance to the surface and promote the interfacial charge separation. Hence, to sum up, the construction of the unique hierarchical CPB/TiO_2 structure greatly enhances the photocatalytic performance due to the existence of TiO_2 nanoflakes, which (1) greatly prohibits the aggregation of the $CsPbBr_3$, forming much smaller perovskite particles that shorten the charge transfer distance; (2) heightens light absorption by the multiple reflection and scattering between the nanoflakes structure that benefits the solar energy harvesting and conversion; (3) enhances the adsorption of toluene molecules and promotes the surface reaction rates.

Photocatalytic Mechanism

To elucidate the photocatalytic mechanism of toluene oxidation over the CPB/TiO_2 photocatalyst, a series of control experiments have been conducted in the absence of O_2 or with the addition of specific radical scavengers. As shown in **Fig. 8a**, the toluene oxidation is almost completely suppressed when O_2 is replaced by Ar, indicating that O_2 is indispensable. When isopropanol (IPA) is added into the reaction system as a scavenger of hydroxyl radicals (•OH), it has almost no effect on toluene conversion, suggesting that •OH is rarely involved in the reaction. In contrast, whether adding ammonium oxalate (AO) to eliminate holes (h^+) or butylated hydroxytoluene (BHT) to capture carbon-centered radicals, the reaction rate significantly reduces. Besides, the toluene conversion is also significantly decreased when BQ is added as superoxide free radical (•O_2^-) scavenger. The above results clearly indicate that •O_2^-, h^+, and carbon-centered radicals play key roles in the photocatalytic selective oxidation of toluene.

Subsequently, to further identify the existence of •O_2^-, electron paramagnetic resonance (EPR) spectroscopy was employed using 5,5-dimethyl-pyrroline-N-oxide (DMPO) as a trapping agent. As shown in **Fig. S12†** and **Fig. 8b**, no DMPO-•O_2^- signal is detected in dark condition. After visible light irradiation, distinct signals of DMPO-•O_2^- are observed for both $CsPbBr_3$ and CPB/TiO_2, while no signals are detected from TiO_2. The CPB/TiO_2 catalyst exhibits a higher ability to generate more •O_2^- radicals than pure $CsPbBr_3$, which is important to promote

the oxidation of toluene. Moreover, no DMPO-•OH signal is observed under the same conditions, demonstrating that •OH is absent in the reaction process (**Fig. S13† and S15†**).
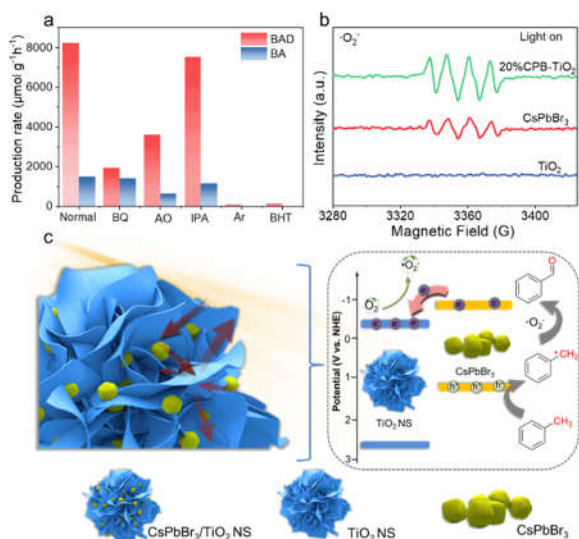
Fig. 8. (a) Photocatalytic toluene oxidation in the absence or presence of various radical scavengers. (b) EPR spectra of DMPO-•O$_2^-$. (c) Schematic illustration of the proposed mechanism of photocatalytic oxidation of toluene over the CPB/TiO$_2$ composite.

Based on the above analyses, a possible photocatalytic reaction mechanism over the hierarchical CPB/TiO$_2$ heterojunction is proposed. As schematically illustrated in **Fig. 8c,** Upon the photoexcitation, electrons and holes are generated in the conduction band (CB) and the valence band (VB) of CsPbBr$_3$. Due to the staggered energy bands, the photogenerated electrons in the CB of CsPbBr$_3$ can efficiently migrate to the CB of TiO$_2$ and left holes on the VB of CsPbBr$_3$, which prolongs the lifetime of the photogenerated charge carriers. After that, molecular O$_2$ can be activated by electron on the CB of TiO$_2$. Meanwhile, photogenerated holes oxidize the toluene to produce benzyl radicals (·CH$_2$-R) on the VB of CsPbBr$_3$. Then, the •O$_2^-$ radical reacts with the benzyl radicals to produce benzaldehyde.

Conclusions

In summary, we have designed and synthesized a hierarchical CPB/TiO$_2$ heterojunction as advanced photocatalyst for efficient visible-light-driven toluene oxidation by assembling CsPbBr$_3$ nanoparticles onto nanoflower-shaped TiO$_2$ with 2D nanoflakes subunits. The formed CPB/TiO$_2$ composite integrates the structural and electronical merits of the nanoflower-shaped TiO$_2$ and halide perovskite CsPbBr$_3$, which not only enhances the solar light utilization, but also enhances the adsorption of toluene reactant, and boosts the separation and transportation of photogenerated carriers. A high toluene oxidation rate of 10200 µmol g^{-1} h^{-1} is achieved over the optimal CPB/TiO$_2$ composite, which is about 20-fold higher than that of blank CsPbBr$_3$. The study demonstrates the significance of rational design of well-defined hierarchical heterojunction catalysts over metal halide perovskites for efficient photocatalytic redox reaction.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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