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# Room-temperature persistent luminescence in metal halide perovskite nanocrystals for solar-driven CO<sub>2</sub> bioreduction

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## Abstract

The rapid crystal growth of metal halide perovskite (MHP) nanocrystals inevitably leads to the generation of abundant crystal defects in the lattice. Here, defects-mediated long-lived charges and accompanied room temperature persistent luminescence is demonstrated to be a general phenomenon in MHP nanocrystals. Density functional theory (DFT) calculations suggest that the collaboration of Schottky and point defects enables cascade upward depletion for electron transfer in MHP nanocrystals, leading to the generation of long-lived photo-excited charges with lifetimes over 30 min. The excellent optical properties including the presence of long-lived charges, high charge separation efficiency, and broad absorption in the visible region make MHPs ideal candidates for both photocatalysis and photo-biocatalysis. The MHPs were further integrated with enzymes to construct a light-driven biosynthetic system for the selective production of fine chemicals from CO<sub>2</sub> with solar energy. The biosynthetic system can produce formate with a quantum yield of 3.24%, much higher

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5 than that of plants (~0.2-1.6%). These findings will benefit the understanding of the optoelectronic properties  
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7 of MHPs and further provide opportunities for the development of biosynthetic systems for solar-to-chemical  
8  
9 synthesis.

## 11 12 **Keywords**

13  
14 persistent luminescence, nanoparticles, metal halide perovskites, defects, CO<sub>2</sub> reduction  
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## 17 18 **Introduction**

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20 Metal halide perovskites (MHPs) have emerged as a fascinating class of semiconductors with superior  
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22 optoelectronic properties including large light absorption coefficient, high charge mobilities, long charge  
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24 diffusion length, and tunable bandgaps.<sup>1-4</sup> In the past years, high-performance optoelectronics such as solar  
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26 cells,<sup>5-7</sup> light-emitting diodes (LEDs),<sup>8</sup> lasers,<sup>9</sup> and photodetectors,<sup>1,2,10</sup> have been developed based on MHPs.<sup>4,11</sup>  
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28 Within the short time since their development, perovskite solar cells have achieved power conversion  
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30 efficiencies approaching that of commercialized polycrystalline silicon photovoltaics.<sup>1,12</sup> The optoelectronic  
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32 properties of MHPs are highly correlated with their lattice structures.<sup>13-15</sup> Researchers showed that regulating  
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34 the lattice structures in MHPs by means such as doping<sup>13-15</sup> can change the crystalline structure, electronic  
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36 structure, bandgap, and crystallinity of MHPs, leading to controllable quantum yields,<sup>8</sup> increased charge  
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38 transport, and stability.<sup>14-17</sup> The lattice structure is one of the chief factors that determine the optoelectronic  
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40 properties of MHPs.  
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44 Defects, the ubiquitous lattice structures in solid materials, are deviations or disruptions in the continuity of  
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46 the regular arrangement of atoms.<sup>18</sup> The most exciting feature of MHPs is their defect-tolerance,<sup>1,2,4</sup> indicating  
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48 the presence of a large number of defects in MHPs.<sup>19,20</sup> Generally, the rapid crystal growth of MHPs inevitably  
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50 leads to the generation of abundant defects in the lattice, such as vacancies and interstitials.<sup>1,4,21</sup> Defects in  
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52 semiconductors have always been of paramount importance as they control the optoelectronic performance  
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54 of these materials in applications.<sup>22,23</sup> The presence of defects can form transition levels in the bandgap and  
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5 change the absorption/emission properties of semiconductors, leading to a substantial enhancement of the  
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7 photoluminescence quantum yields or red-shift of the emission peaks.<sup>23,24</sup> Also, defects can trap free charges  
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9 and lead to the generation of long-lived charges with lifetimes up to hours.<sup>23,25,26</sup> The long-lived charges can  
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11 recombine to produce persistent luminescence<sup>26-28</sup> or be transported to the surface of the semiconductors for  
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13 photocatalysis.<sup>23</sup> The large number of unavoidable defects in MHPs also leads to modification of their bandgaps  
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15 and the entrapment of free charges; that is, the defects empower MHPs with undiscovered optoelectronic  
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17 properties.  
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21 Herein, we report that the intrinsic defects in MHPs can lead to long-lived charge separation and the  
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23 persistent luminescence phenomenon, and the MHPs were integrated with enzymes for the selective  
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25 production of fine-chemical from CO<sub>2</sub>. Persistent luminescence was observed as a general phenomenon in  
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27 MHPs due to the recombination of the long-lived charges after excitation ceases. The formation of different  
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29 defects in CsPbBr<sub>3</sub> was studied with density functional theory (DFT) calculations, which indicated that  
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31 collaboration of Schottky defects and point defects supports the formation of long-lived charges based on the  
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33 broad distribution of occupied energy levels within the bandgap. A light-driven biosynthetic system was further  
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35 constructed for the production of fine chemicals from CO<sub>2</sub> based on CsPbBr<sub>3</sub> and enzymes. This biosynthetic  
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37 system can produce formate from CO<sub>2</sub> continuously over light-dark cycles, demonstrating a promising route  
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39 toward solar-to-chemical CO<sub>2</sub> reduction.  
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## 41 42 43 **Experimental Methods**

### 44 45 **Materials.**

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47 Lead(II) chloride (PbCl<sub>2</sub>, 99.99%), lead(II) bromide (PbBr<sub>2</sub>, 99.0%), lead(II) iodide (PbI<sub>2</sub>, 99.9%), caesium  
48  
49 carbonate (Cs<sub>2</sub>CO<sub>3</sub>, 99.9%), bismuth triiodide (BiI<sub>3</sub>, 99.99%), silver nitrate (AgNO<sub>3</sub>, 99.8%), oleic acid (OA, AR),  
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51 1-octadecene (ODE, 80-90%), oleylamine (OLA, AR), hydrobromic acid (HBr, AR, 40%), titanium butoxide (TBOT,  
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53 ≥ 99.0%), triethanolamine (TEOA, AR), 2,2'-bipyridyl (AR, 99.0%), pentamethylcyclopentadienylrhodium (III)

chloride dimer ((Cp\*RhCl<sub>2</sub>)<sub>2</sub>, 99%), and β-nicotinamide adenine dinucleotide (NAD<sup>+</sup>, 97%) were purchased from Aladdin Reagent Co. Ltd (China). Toluene (HPLC grade) was purchased from Thermo Fisher Scientific Inc. Bismuth tribromide (BiBr<sub>3</sub>, 99%) was purchased from Alfa Aesar Chemical Co. Ltd. Methanol (AR, ≥ 99.7%), ethyl acetate (AR, ≥ 99.5%), n-hexane (AR, ≥ 97.0 %), and diethyl ether (AR, ≥ 99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Formate dehydrogenase from *Candida boidinii* (CbFDH) and formate assay kit were purchased from Sigma-Aldrich Co., LLC.

### Characterization.

The sizes and shapes of nanocrystals were determined by a JEM-2100 transmission electron microscope (TEM, JEOL). The elemental mappings were conducted on a JEOL JEM-2100F TEM working at 200 kV. The shapes and elemental mappings of p-CsPbBr<sub>3</sub> were characterized by a Zeiss Merlin Compact scanning electron microscope (SEM). Powder X-ray diffraction (XRD) characterization was conducted on a Bruker D8 Advance X-ray diffractometer using Cu-Kα radiation (wavelength, λ = 1.5406 Å). Absorption spectra of nanocrystals were collected with a Shimadzu UV-2550 UV-Vis spectrophotometer. Photoluminescence spectra of nanocrystals were measured on a Hitachi F-4600 fluorescence spectrometer. The afterglow luminescence in the CsPbBr<sub>3</sub> nanocrystal powder was collected on a HORIBA Scientific spectrometer, Fluorolog-3-ultrafast with 450 W xenon lamp, double mono in ex side, single mono (with H10330 NIR PMT as T-side) and iHR320 (with PPD-850 and CCD as L-side) in Em sides. The photoluminescence decay spectra were recorded on an Edinburgh FLS980 spectrometer using the time-correlated single-photon counting mode. X-ray photoelectron spectroscopy (XPS) was analyzed using a Thermo Escalab 250Xi instrument equipped with Al Kα monochromatized X-rays at 1,486.6 eV. The photoluminescence and persistent luminescence photos and videos were taken with a Nikon D3000 single-lens digital camera and a portable ZF5 UV lamp was used as the excitation source.

### DFT calculations.

The CASTEP package within DFT was applied to perform the theoretical calculations for CsPbBr<sub>3</sub>.<sup>29</sup> The GGA with PBE was employed to show the exchange-correlation energy in all of the calculations.<sup>30,31</sup> The ultra-soft

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4 pseudopotential (cut-off energy, 310 eV) was used. The Broyden-Fletcher-Goldfarb-Shannon (BFGS) algorithm  
5 was employed to converge the Hellmann-Feynman forces to less than 0.001 eV/Å for all geometry  
6 optimization.<sup>32</sup> Guided by the initial convergence test, Monkhost-Pack reciprocal space integration was  
7 conducted with coarse k-points in consideration of the DFT computational cost.<sup>33</sup> The ultra-fine convergence  
8 criteria were set according to the tolerances of the inter-ionic displacement and the total energy did not exceed  
9  $5 \times 10^{-3}$  Å per atom and  $5 \times 10^{-5}$  eV per atom, respectively.  
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### 18 **Measurement of the afterglow decay images.**

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20 A colloidal mixture of nanocrystals in n-hexane was placed in a 48-well plate. A portable ZF5 UV lamp was used  
21 as the excitation source. After illumination for 3 min, the decay images were recorded by using the IVIS Lumina  
22 XR Imaging System (Caliper, USA).  
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### 28 **Photoelectrochemical measurement.**

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30 The photoelectrochemical properties of p-CsPbBr<sub>3</sub> nanocrystals were measured on a CHI Model 618 C  
31 electrochemical workstation. A standard three-electrode system was used: FTO glass coated with p-CsPbBr<sub>3</sub>  
32 nanocrystals as the working electrode, Pt plate as the counter electrode, and Ag/AgCl as the reference  
33 electrode. The 0.5 M Na<sub>2</sub>SO<sub>4</sub> electrolyte solution was purged with high purity argon for 30 min before each  
34 measurement. The photocurrent curves were recorded using a 300 W xenon lamp with switch on-off cycles.  
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### 42 **Synthesis of Cs-oleate.**

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44 A stock solution of Cs-oleate was synthesized following the reported synthesis procedure.<sup>34</sup> Briefly, 0.8145 g of  
45 Cs<sub>2</sub>CO<sub>3</sub> (2.5 mmol), 2.5 mL of OA, and 40 mL of ODE were added to a 100 mL flask, followed by drying at 120 °C  
46 for 1 h under vacuum. After that, the solution in the flask was heated to 150 °C under argon gas. The solution  
47 became clear and the obtained Cs-oleate was collected for further use.  
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### 53 **Synthesis of CsPbX<sub>3</sub> nanocrystals.**

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5 The CsPbX<sub>3</sub> perovskite nanocrystals were prepared according to a previously reported hot-injection method.<sup>6</sup>  
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7 Briefly, 10 mL of ODE, and 0.38 mmol of PbX<sub>2</sub> were added to a 50 mL three-neck round bottom flask, followed  
8  
9 by drying for 1 h at 120 °C under vacuum. Then 1 mL of OLA and 1 mL of OA were injected into the above  
10  
11 solution at 120 °C under argon gas. After PbX<sub>2</sub> was dissolved completely, the solution in the flask was heated  
12  
13 to 160 °C. Then 1 mL of Cs-oleate solution pre-heated to 100 °C was quickly injected into the mixture. After 10  
14  
15 s of reaction, the flask was transferred to an ice-water bath for rapid cooling. The CsPbX<sub>3</sub> nanocrystals were  
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17 collected by centrifugation.  
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#### 19 20 21 **Synthesis of Cs<sub>2</sub>AgBiBr<sub>6</sub> nanocrystals.**

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23 The Cs<sub>2</sub>AgBiBr<sub>6</sub> nanocrystals were synthesized according to a reported procedure.<sup>35</sup> Briefly, 45 mg of BiBr<sub>3</sub>, 17  
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25 mg of AgNO<sub>3</sub>, 0.1 mL of HBr, 4 mL of ODE, 1 mL of OA, and 1 mL of OLA were loaded into a 25 mL three-neck  
26  
27 round bottom flask and were heated to 120 °C for 1 h under vacuum. After that, the solution was heated to  
28  
29 200 °C in argon gas and 0.8 mL of pre-heated Cs-oleate stock solution (100 °C) was quickly added into the  
30  
31 solution under vigorous stirring. The color of the mixture quickly turned from yellow-green to yellow. A few  
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33 seconds later, the flask was rapidly placed in an ice-water bath for cooling. The obtained Cs<sub>2</sub>AgBiBr<sub>6</sub>  
34  
35 nanocrystals were collected by centrifugation and re-dispersed in n-hexane.  
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#### 38 39 **Synthesis of Cs<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> nanocrystals.**

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41 The Cs<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> nanocrystals were synthesized by a reported protocol.<sup>36</sup> The Cs-oleate precursor and the BiI<sub>3</sub>  
42  
43 precursor were synthesized firstly. OA (1.5 mL), ODE (20 mL) and Cs<sub>2</sub>CO<sub>3</sub> (0.45 g) were added to a 50 mL three-  
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45 neck round bottom flask. The mixture was heated to 130 °C for 1 h with stirring under vacuum to form a clear  
46  
47 colloidal Cs-oleate precursor. After that, OA (1.5 mL), OLA (1.5 mL), ODE (15 mL), and BiI<sub>3</sub> (330 mg) were added  
48  
49 to a 50 mL three-neck round bottom flask. The mixture was dried under vacuum for 1 h at 90 °C to generate a  
50  
51 yellow colloidal BiI<sub>3</sub> precursor. In a typical procedure, 2 mL of BiI<sub>3</sub> precursor in a glass vial was heated at 100 °C  
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53 for 5 min. Then 0.1 mL of the pre-heated Cs-oleate solution was quickly added to the above solution. After  
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5 about 40 s of reaction, the solution changed from yellow to deep orange, indicating the formation of Cs<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>  
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7 nanocrystals. The Cs<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> nanocrystals were separated by centrifugation and re-dispersed in n-hexane.  
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### 10 **Synthesis of p-CsPbBr<sub>3</sub> nanocrystals.**

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12 The p-CsPbBr<sub>3</sub> nanocrystals were synthesized following the reported method.<sup>37</sup> First, the TBOT solution was  
13  
14 prepared by dissolving 20 μL TBOT in 1 mL toluene and the solution was added dropwise to 10 mL of CsPbBr<sub>3</sub>  
15  
16 solution (about 2 mg/mL toluene) in a 50 mL centrifuge tube under stirring. The obtained solution was stirred  
17  
18 at room temperature for hydrolysis until the clear solution became cloudy. After 3 h of reaction, the precipitate  
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20 was separated by centrifugation, followed by drying at room temperature for 1 h and 80 °C overnight under  
21  
22 vacuum. Subsequently, the dried yellow product was calcined at 300 °C for 5 h under argon flow. Finally, the  
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24 p-CsPbBr<sub>3</sub> nanocrystals were ground in an agate mortar and stored in a centrifuge tube for further use.  
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### 28 **Preparation of [Cp\*Rh(bpy)H<sub>2</sub>O]<sup>2+</sup>.**

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30 Briefly, 30.90 mg of entamethylcyclopentadienylrhodium (III) chloride dimer (Cp\*RhCl<sub>2</sub>)<sub>2</sub> was suspended in 4  
31  
32 mL of methanol and a red suspension was formed. Then 15.62 mg of 2,2'-bipyridyl was added to the red  
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34 suspension and a clear yellowish solution was obtained after a few minutes. The above yellowish solution was  
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36 concentrated to about 1 mL by rotary evaporation. After that, [Cp\*Rh(bpy)Cl]Cl was collected by adding diethyl  
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38 ether to the concentrated solution at 4 °C and dried under vacuum conditions. A stock solution of  
39  
40 [Cp\*Rh(bpy)(H<sub>2</sub>O)]<sup>2+</sup> (50 mM) was prepared by adding [Cp\*Rh(bpy)Cl]Cl to 1 mL of water and stored at 4 °C in  
41  
42 the dark.  
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### 46 **Photocatalytic regeneration of NADH.**

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48 The photocatalytic reduction of NAD<sup>+</sup> into NADH was conducted in a quartz reactor and a 450 nm LED (50 W)  
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50 was used to excite the solution. The photocatalytic reaction system (1 mL) contained 1 mM of NAD<sup>+</sup>, 0.125 mM  
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52 of [Cp\*Rh(bpy)H<sub>2</sub>O]<sup>2+</sup>, 2 M of TEOA, 0.5 mg/mL p-CsPbBr<sub>3</sub> and 100 mM phosphate buffer (PB, pH 7.5). The  
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54 reaction system was incubated for 10 min in darkness before being illuminated by a 450 nm LED. The  
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5 concentration of the regenerated NADH was determined by UV-Vis spectrophotometry using  $6220 \text{ M}^{-1} \text{ cm}^{-1}$  as  
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7 the extinction coefficient of NADH at 340 nm. To optimize the catalytic performance of p-CsPbBr<sub>3</sub> nanocrystals,  
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9 the pH values, sacrificial reagents, and the concentration of TEOA and [Cp\*Rh(bpy)H<sub>2</sub>O]<sup>2+</sup> were manipulated.  
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### 11 12 **Long persistent photocatalytic regeneration of NADH.**

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14 The long persistent photocatalytic production of NADH was conducted with a similar protocol. First, p-CsPbBr<sub>3</sub>  
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16 or TiO<sub>2</sub> nanoparticles (2 mg) dispersed in 0.2 mL of PB buffer (100 mM, pH 7.5) was illuminated by a 50 W 450  
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18 nm LED lamp for 2 h. Then, the irradiated solution was added to a reaction system composed of 1 mM of NAD<sup>+</sup>,  
19  
20 0.125 mM of [Cp\*Rh(bpy)H<sub>2</sub>O]<sup>2+</sup>, 2 M of triethanolamine, and PB buffer. The final volume of the reaction  
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22 system was 1 mL. The reaction system was incubated in the dark and the amount of the regenerated NADH  
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24 was determined by UV-Vis spectrophotometry.  
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### 27 28 **Biosynthesis of formate from CO<sub>2</sub>.**

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30 Briefly, the biosynthesis of the formate was conducted in a glass vial bubbled with CO<sub>2</sub> gas at room temperature,  
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32 and a 50 W 450 nm LED was used as the light source. The reaction solution (2 mL) containing 2 mg/mL p-  
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34 CsPbBr<sub>3</sub> or TiO<sub>2</sub> nanoparticles, 5 mM NAD<sup>+</sup>, 0.125 mM of [Cp\*Rh(bpy)H<sub>2</sub>O]<sup>2+</sup>, 2 M of triethanolamine, 2 mg/mL  
35  
36 CbFDH and 100 mM PB buffer (pH 7.5) was bubbled with CO<sub>2</sub> gas. After illumination with a 450 nm LED for the  
37  
38 designated time, the supernatant was collected by centrifugation. The concentration of formate in the  
39  
40 supernatant was detected with the formate assay kit.  
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### 43 44 **Biosynthesis of formate from CO<sub>2</sub> in light-dark cycles.**

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46 The biosynthesis of formate with a light-dark cycle was carried out similarly to the above reaction. For the  
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48 biosynthesis reaction under light illumination, a reaction system (2 mL) containing 2 mg/mL p-CsPbBr<sub>3</sub>, 5 mM  
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50 NAD<sup>+</sup>, 0.125 mM of [Cp\*Rh(bpy)H<sub>2</sub>O]<sup>2+</sup>, 2 M of triethanolamine, and 100 mM PB buffer (pH 7.5) was loaded  
51  
52 into a glass vial and illuminated with 450 nm LED lamp for a certain time. For the dark stage, 4 mg of CbFDH  
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54 was added to the obtained solution and the solution was bubbled with CO<sub>2</sub> gas in dark at room temperature.  
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The formate concentration was monitored by a formate assay kit. The artificial photosynthesis of the formate with four light-dark cycles was performed in a glass vial bubbled with CO<sub>2</sub> gas under the same reaction conditions.

#### Average photoluminescence lifetime calculation.

The transient photoluminescence decay curves of CsPbBr<sub>3</sub> and p-CsPbBr<sub>3</sub> nanocrystals were fitted with a triplet exponential function of  $Y(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3) + y_0$  and the average photoluminescence lifetime ( $\tau$ ) of CsPbX<sub>3</sub> and p-CsPbBr<sub>3</sub> nanocrystals were calculated from equation 1:

$$\tau = \frac{A_1 \tau_1^2 + A_2 \tau_2^2 + A_3 \tau_3^2}{A_1 \tau_1 + A_2 \tau_2 + A_3 \tau_3} \quad (1)$$

#### Quantum yield calculation.

According to a previous study, the formate production quantum yield was calculated by the ratio of the effective electrons used for formate production to the total input photon flux:<sup>38</sup>

$$\text{quantum yield (\%)} = \frac{2 \times \text{mol of formate}}{\text{mol of total photons}} \times 100\% \quad (2)$$

where

mol of formate generated = the total formate concentration  $\times$  total volume

mol of total photons = photo flux  $\times$  area of illumination  $\times$  reaction time / Avogadro's Number ( $N_A$ )

And photo flux was estimated by equation 3:

$$\text{photo flux} = \frac{P \times \lambda}{h \times c} \quad (3)$$

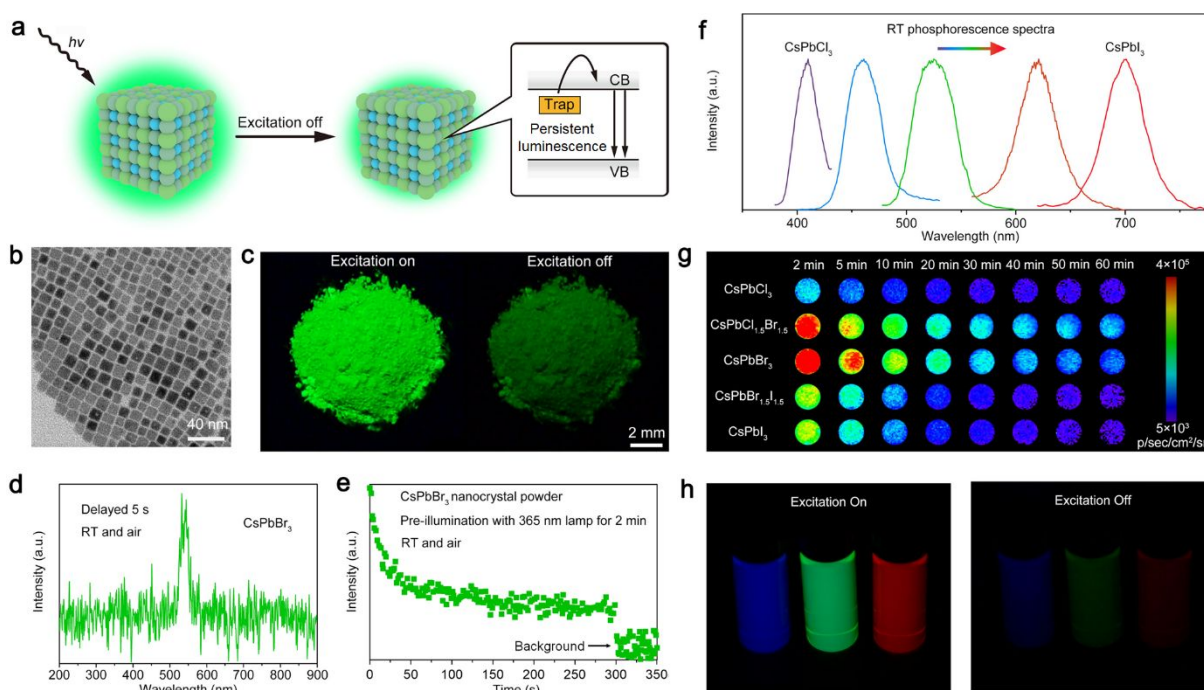
Where  $P$  is the power of the LED light,  $\lambda$  is the emission wavelength of the LED light,  $h$  is the Planck constant ( $6.63 \times 10^{-34}$  J·s),  $c$  is the speed of light ( $3.00 \times 10^8$  m·s<sup>-1</sup>).

## Results and Discussion

### The general persistent luminescence phenomenon in MHP nanocrystals.

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5 The defect-tolerance virtue of MHPs suggests the presence of abundant defects in MHPs.<sup>1,2,4</sup> Considering the  
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7 unique charge-trapping feature of crystal defects, we reason that the long-lived charges and the accompanied  
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9 persistent luminescence occur in MHPs, as illustrated in Figure 1a. The classic cubic CsPbBr<sub>3</sub> nanocrystals<sup>34</sup>  
10  
11 (Figure 1b) were first tested. As shown in Figure 1c, green persistent luminescence is observed from the  
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13 CsPbBr<sub>3</sub> nanocrystal powder at room temperature after removing the 365 nm UV illumination (Video S1).  
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15 Figure 1d further shows that obvious persistent luminescence at around 536 nm was detected in CsPbBr<sub>3</sub>  
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17 nanocrystals even at a 5 s delay after photoexcitation at room temperature. We further recorded the persistent  
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19 luminescence decay in CsPbBr<sub>3</sub> nanocrystals over time. Persistent luminescence with persistent time over 300  
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21 s was detected in CsPbBr<sub>3</sub> nanocrystals (Figure 1e), suggesting the presence of long-lived charges in CsPbBr<sub>3</sub>.  
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23 These results confirm that long-lived charges and the accompanied persistent luminescence occur in the  
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25 CsPbBr<sub>3</sub> nanocrystals.  
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30 We next asked whether persistent luminescence is a general phenomenon in MHP nanocrystals. A series of  
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32 perovskite nanocrystals was further tested, including CsPbX<sub>3</sub> (X= Cl-I),<sup>34</sup> Cs<sub>2</sub>AgBiBr<sub>6</sub><sup>35</sup> and Cs<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub><sup>36</sup> (Figures S1-  
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34 S8). The persistent luminescence feature of these perovskite nanocrystals was tested. Figure 1f presents the  
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36 room-temperature phosphorescence spectra of the MHP nanocrystals. Long-lifetime emissions were observed  
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38 over the entire visible spectral region from the MHP nanocrystal dispersions, indicating the persistent  
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40 luminescence feature of these nanocrystals. The persistent luminescence in the MHP nanocrystals was further  
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42 studied using the IVIS Spectrum imaging system<sup>39</sup> in the bioluminescence mode. After pre-charging with a 365  
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44 nm UV lamp for 2 min, all of the MHP nanocrystals displayed strong persistent luminescence after excitation  
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46 ceases (Figure 1g and Figure S9). The decay images in Figure 1g show that the persistent luminescence  
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48 intensities of the MHP nanocrystals decreased slowly and that obvious persistent luminescence was still  
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50 detected after 1 h of decay. Photographs of CsPbX<sub>3</sub> colloidal dispersions during and after excitation at room  
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52 temperature show obvious persistent luminescence (Figure 1h and Video S2). These assays demonstrate that  
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54 the long-lived charges and the accompanied persistent luminescence are a general phenomenon in MHPs.  
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**Figure 1** | *Persistent luminescence in MHP nanocrystals. a*, Schematic representation for the persistent luminescence in MHP nanocrystals. *b*, TEM image of the CsPbBr<sub>3</sub> nanocrystals. *c*, Photographs of CsPbBr<sub>3</sub> nanocrystal powder during and after excitation. *d*, Room-temperature persistent luminescence spectrum of the CsPbBr<sub>3</sub> nanocrystals with a delay time of 5 s. *e*, persistent luminescence decay curve of the CsPbBr<sub>3</sub> nanocrystals pre-excited by a UV lamp for 2 min. *f*, Room-temperature phosphorescence spectra of the MHP nanocrystals with varying halide compositions. *g*, persistent luminescence decay images in MHP nanocrystals. *h*, Photographs of CsPbCl<sub>1.5</sub>Br<sub>1.5</sub>, CsPbBr<sub>3</sub> and CsPbBr<sub>1.5</sub>I<sub>1.5</sub> colloidal dispersions during and after excitation.

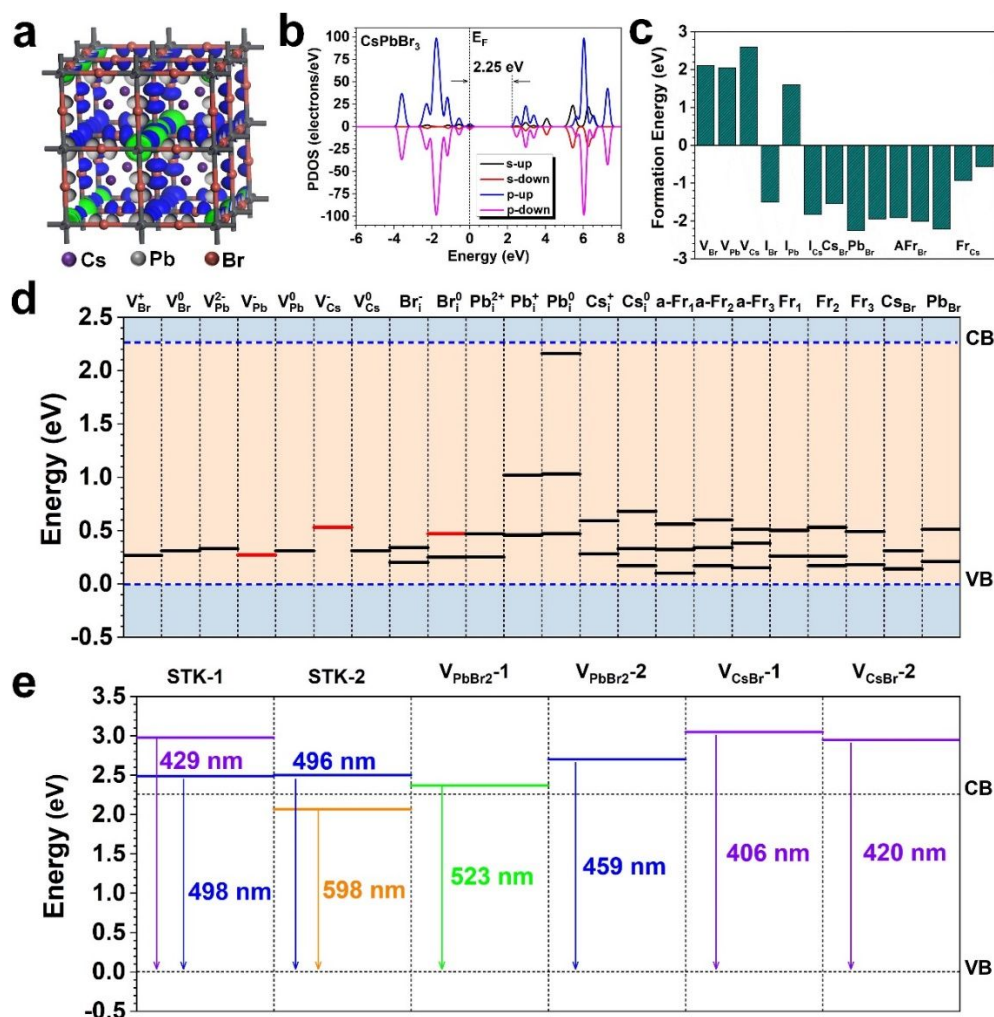
### The origin of the persistent luminescence phenomenon in MHP nanocrystals.

The persistent luminescence originates from the slow escape and recombination of the charges trapped by defects MHP nanocrystals after excitation ceases. The formation of defects in CsPbBr<sub>3</sub> and their influences on charge separation were further systematically studied *via* their electronic structures. In CsPbBr<sub>3</sub> crystal, both the bonding and anti-bonding orbitals near the Fermi level ( $E_F$ ) are predominantly contributed by Pb (Figure 2a). The Br sites also display the electron-rich feature while Cs atoms show a limited contribution to the electronic distribution (Figure 2a). From the projected density of states, the conduction band minimum (CBM) and valence band maximum (VBM) are both mainly composed of the p-orbitals from Pb-6p and Br-4p (Figure 2b). Previous studies demonstrate the presence of both defects-related shallow and deep trap states in MHPs.<sup>19,20</sup> The formation of commonly encountered native defects such as vacancies and their influence on

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4 the optical properties of CsPbBr<sub>3</sub> was systematically studied with DFT calculations. For the formation of point  
5 defects in CsPbBr<sub>3</sub> crystals, the pure vacancies show slightly higher energy costs while the antisite and Frenkel  
6 defects are thermodynamically favorable, indicating the presence of unavoidable defects in CsPbBr<sub>3</sub> crystals  
7 during synthesis (Figure 2c). The single-particle levels of intrinsic defects in CsPbBr<sub>3</sub> with different charge states  
8 are further summarized. Figure 2d indicates that the point defects are responsible for the formation of the hole  
9 traps near the VBM. For the Pb vacancy ( $V_{Pb}$ ), the occupied states are noted in both  $V_{Pb}^0$  and  $V_{Pb}^{2-}$ , which are  
10 0.31 eV and 0.33 eV above the VBM, respectively. Meanwhile, an empty state at 0.27 eV above the VBM is  
11 identified in the neutral  $V_{Pb}^-$ , which can alleviate the energy barrier for electron transfer from the conduction  
12 band. The additional gap states for  $V_{Cs}^0$  and  $V_{Cs}^-$  are noticed at 0.53 and 0.31 eV above the VBM, respectively.  
13 In particular, we notice the ladder-like distributions of occupied states from  $Pb_i^0$  to  $Pb_i^{2+}$ , which varies from  
14 the range of 0.5 eV to 2.16 eV above the VBM. These states have supplied the non-equilibrium intrinsic charge  
15 states to prolong the luminescence performance after excitation. Moreover, large amounts of occupied states  
16 have been formed within the range of 0.6 eV by both the anion and cation Frenkel defects. Therefore, we  
17 propose the cascade upward depletion mechanism facilitated by high energy levels of defects from the  
18 synthesis. Under excitation, electrons trapped in these states can tunnel through the conduction band to  
19 realize de-excitation and accompanying persistent luminescence.  
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40 Besides the simple point defects, Schottky and Schottky-like defects were further investigated in  
41 agglomerated and separated types (Figure 2e). Both the Schottky defects and the Schottky-like defect such as  
42 PbBr vacancy ( $V_{PbBr2}$ ) introduce empty gap states above the VBM. For instance, for the agglomerated STK  
43 defects (STK-1), two additional electron traps are formed at the CBM, which locate at 2.49 and 2.89 eV above  
44 VBM, respectively. These two electron traps correspond to photon emission of 498 (violet) and 429 nm (blue),  
45 which are close to the experimental results. Similar to the agglomerated STK, the separated STK defect also  
46 demonstrate two-gap states at 2.50 and 2.07 eV above VBM, supporting the photoemission of 496 (blue) and  
47 598 nm (orange), respectively. These additional empty states not only act as electron traps but also promote  
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cascade upward depletion-based electron transfer by supplying the appropriate energy levels over the CBM. Therefore, combined with the cascade upward depletion by point defects, the intrinsic defects can lead to the generation of long-lived charges and persistent luminescence in CsPbBr<sub>3</sub> crystals. In addition to the intrinsic defects, introducing exogenous defects by means such as hetero-valence doping during preparation can further enhance the intensity and prolong the decay time of persistent luminescence in MHPs.<sup>25,27</sup>

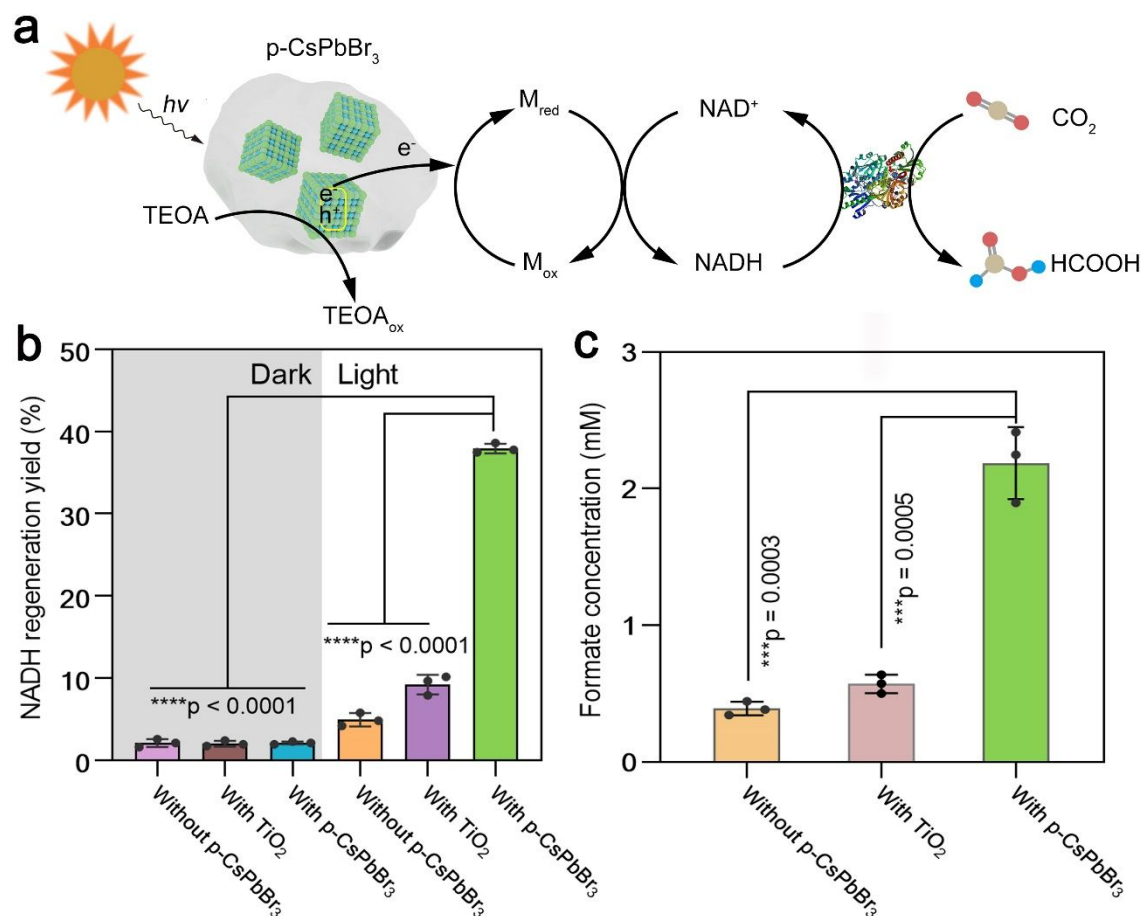


**Figure 2** | The origin of persistent luminescence in CsPbBr<sub>3</sub>. **a**, The bonding and anti-bonding orbitals of CsPbBr<sub>3</sub>. Purple balls, Cs; Dark Grey balls, Pb; Brown balls, Br; Blue isosurface, bonding orbitals; green isosurface, anti-bonding orbitals. **b**, The projected density of states of CsPbBr<sub>3</sub>. **c**, Formation energies of point defect in CsPbBr<sub>3</sub>. **d**, The summarized single-particle levels of simple point defects of CsPbBr<sub>3</sub> in both charged and neutral states (Empty states = red; Occupied states = black). **e**, The summarized single-particle levels of Schottky and Schottky-like defects of CsPbBr<sub>3</sub> in agglomerated and separation types. STK-1, V<sub>PbBr2</sub><sup>-1</sup>, and V<sub>CsBr</sub><sup>-1</sup> are the agglomerated type, and STK-2, V<sub>PbBr2</sub><sup>-2</sup> and V<sub>CsBr</sub><sup>-2</sup> are the separated type of defects.

### Light-driven biosynthesis of formate from CO<sub>2</sub> based on MHPs.

The presence of long-lived charges, efficient charge separation, and broad visible absorption strongly indicate the potential application of MHP nanocrystals in photocatalysis and solar-to-chemical synthesis.<sup>38,40-43</sup> A light-driven biosynthetic system with a simple electron conduit was further constructed for the production of fine chemicals from CO<sub>2</sub> based on CsPbBr<sub>3</sub> nanocrystals and enzymes (Figure 3a). This biosynthetic system integrates the highly efficient light-harvesting ability and long-lived charges of CsPbBr<sub>3</sub> nanocrystals with the highly specific CO<sub>2</sub>-processing capability of enzymes.<sup>38,44,45</sup> The CsPbBr<sub>3</sub> nanocrystals were passivated by a TiO<sub>2</sub> shell (named as p-CsPbBr<sub>3</sub>)<sup>37</sup> to protect CsPbBr<sub>3</sub> from degradation and to facilitate charge transfer (Figures S10-S12). Compared to CsPbBr<sub>3</sub>, the p-CsPbBr<sub>3</sub> shows a faster photoluminescence decay and weaker persistent luminescence intensities, suggesting the efficient transfer of electrons from CsPbBr<sub>3</sub> to the TiO<sub>2</sub> shell (Figures S13 and S14). Under visible light, the generated long-lived electrons in CsPbBr<sub>3</sub> nanocrystals pass through TiO<sub>2</sub> and reach the electron shuttle [Cp\*Rh(bpy)H<sub>2</sub>O]<sup>2+</sup> (Figures S15 and S16). The reduced form electron shuttle [Cp\*Rh(bpy)]<sup>+</sup> further shuttles the electrons to β-nicotinamide adenine dinucleotide (NAD<sup>+</sup>), which converts the NAD<sup>+</sup> to the reduced form, NADH, one of the major reducing agents in biosynthesis. The NADH is consumed in the reduction of CO<sub>2</sub> to formate, and the released NAD<sup>+</sup> oxidizes the [Cp\*Rh(bpy)]<sup>+</sup> for the cyclic production of NADH. By this simple electron conduit, the light-driven biosynthetic system can channel the photo-generated electrons from p-CsPbBr<sub>3</sub> to produce NADH for the sustainable conversion of CO<sub>2</sub> into high-value chemicals. As shown in Figure 3b, the light-driven biosynthetic system afforded a much higher NADH regeneration yield compared to the group without the p-CsPbBr<sub>3</sub>. The favorably oriented electron transfer in the light-driven biosynthetic system provides an NADH production rate of 304.5 ± 5.2 μmol g<sup>-1</sup> h<sup>-1</sup>, corresponding to a yield of 37.9 ± 0.6%. Figure 3c further shows a pronounced increase in formate production. Moreover, the light-driven biosynthetic system produced 2.19 ± 0.29 mM formate under visible light illumination for 2 h, much more than the system without p-CsPbBr<sub>3</sub> nanocrystals. Collectively, these results demonstrated that high-value chemicals can be efficiently produced from CO<sub>2</sub> by integrating the MHP

nanocrystals with an established biosynthetic pathway. The developed light-driven biosynthetic system can serve as a promising method to realize solar-to-chemical conversion.



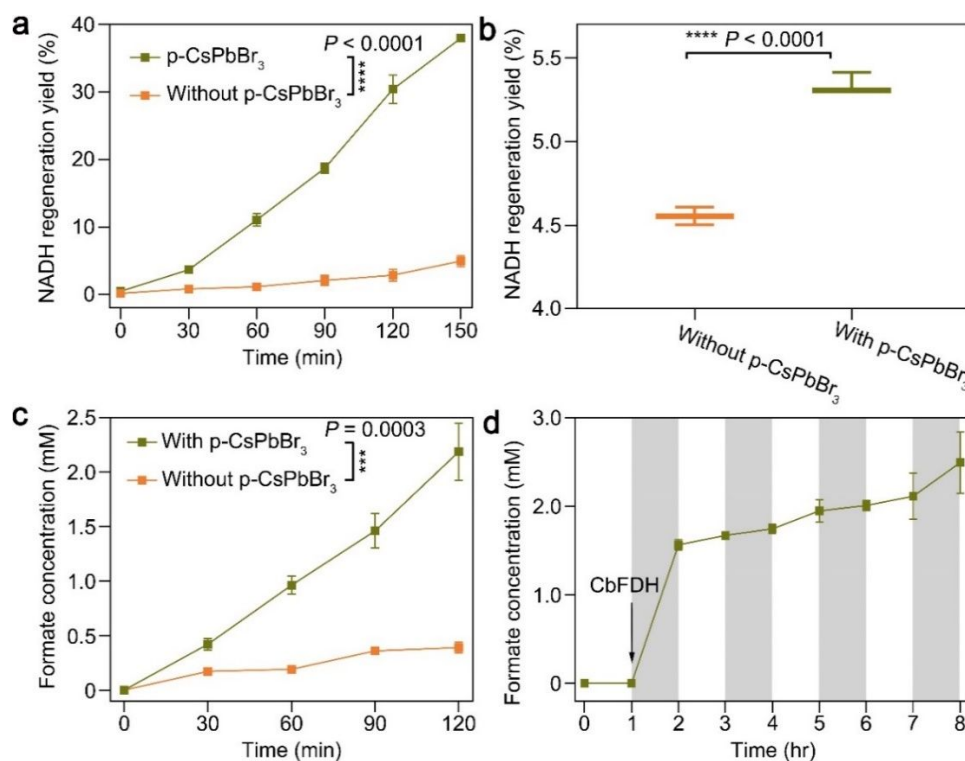
**Figure 3** | Light-driven biosynthesis of formate from  $\text{CO}_2$ . **a**, Schematic illustration of the light-driven biosynthetic system based on  $p\text{-CsPbBr}_3$  and formate dehydrogenase (CbFDH).  $M_{\text{ox}}$ ,  $[\text{Cp}^*\text{Rh}(\text{bpy})\text{H}_2\text{O}]^{2+}$ .  $M_{\text{red}}$ ,  $[\text{Cp}^*\text{Rh}(\text{bpy})]^+$ . TEOA, triethanolamine. **b**, Photocatalytic regeneration of NADH by a 450 nm LED (50 W) illumination. **c**, Production of formate from  $\text{CO}_2$  under LED (50 W) illumination. Error bars show the mean  $\pm$  standard error of the mean (s.e.m.) of three independent measurements.

### NADH and Formate production by the light-driven biosynthetic system.

A series of biosynthetic tests were performed to investigate the NADH and formate generation under light illumination (Figure S17). Transient photocurrent measurement was employed to assay the electron-donating performance of the  $p\text{-CsPbBr}_3$  nanocrystals since electrons transferred out of the  $p\text{-CsPbBr}_3$  could be easily captured by an electrode.<sup>46</sup> Under illumination by a 300 W xenon lamp,  $p\text{-CsPbBr}_3$  produced a robust cathodic



photocurrent with a density of about  $1.33 \mu\text{A cm}^{-2}$ , much higher than that of bare  $\text{TiO}_2$ , showing the good electron-donating feature of  $\text{p-CsPbBr}_3$  (Figure S18). Figure 4a shows that the yield of NADH increased nearly linearly over time under LED (450 nm) illumination, and the yield reached 37.9% within 2.5 h. The NADH regeneration rate was determined to be  $304.5 \pm 5.2 \mu\text{mol g}^{-1} \text{h}^{-1}$ , nearly 769.6% higher than that of the bare  $\text{TiO}_2$  and the control group without the  $\text{p-CsPbBr}_3$  nanocrystals (Figure S19). The NADH regeneration yield increases gradually with the increase of the sacrificial hole scavenger TEOA concentration (Figure S20). The optimal pH for the photogeneration of NADH was determined to be about 7.5 (Figure S20). Moreover, the light-driven biosynthetic system displays good recycling capability in the photo-generation of NADH. Compared to the first cycle, the system retained an NADH regeneration yield of 93% in the tenth cycle (Figure S21), indicating the good reusability of the  $\text{p-CsPbBr}_3$  in the photocatalytic process.



**Figure 4** | The NADH and formate generation in the light-driven biosynthetic system. **a**, Light-driven NADH generation yield over time. **b**, Regeneration of NADH in the dark with pre-illuminated  $\text{p-CsPbBr}_3$  nanocrystals. **c**, Light-driven formate generation vs. time. **d**, Light-driven formate production with light-dark cycles. Error bars show the mean  $\pm$  standard error of the mean (s.e.m.) of three independent measurements.

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5 The MHP nanocrystals can store photon energy within the defects in the form of long-lived charges with a  
6 lifetime of over minutes. Beyond recombination of the trapped charges to produce persistent luminescence,  
7 the trapped charges in p-CsPbBr<sub>3</sub> nanocrystals can also pass to the electron shuttle [Cp\*Rh(bpy)H<sub>2</sub>O]<sup>2+</sup> for the  
8 production of NADH in the dark. The p-CsPbBr<sub>3</sub> nanocrystals pre-illuminated with the LED for 30 min were  
9 added to the biosynthetic system for the conversion of NAD<sup>+</sup> into NADH in the dark. Figure 4b shows that the  
10 reaction system displays obvious NADH generation, indicating that the long-lived electrons in p-CsPbBr<sub>3</sub>  
11 nanocrystals can be used for biosynthesis after excitation ceases. The above findings suggest the special ability  
12 of the MHP nanocrystals in storing the photon energy within defects for photocatalysis in the dark, suggesting  
13 their capability to continuously produce high-value chemicals from CO<sub>2</sub> in the day-night cycles in nature.  
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25 The formate production from CO<sub>2</sub> was further investigated under visible light illumination. As shown in  
26 Figure 4c, the production of formate gradually increased over reaction time in the biosynthetic system, and  
27 the amount of produced formate reached 4.38 μmol after 2 h, affording a formate production quantum yield  
28 of 3.24 ± 0.21%. To further study the formate production capability of the light-driven biosynthetic system, the  
29 system was illuminated with visible light for different times, followed by 1 h of reaction in the dark. The  
30 produced formate increased with the prolonged illumination time (Figure S22), which can be ascribed to the  
31 gradual accumulation of NADH in the biosynthetic system with increasing illumination time. To further study  
32 the photosynthetic behavior, the light-driven biosynthetic system was illuminated in four alternating light-dark  
33 cycles of 1 hour illumination/1 hour dark, to imitate the intermittent nature of the solar source. The  
34 biosynthetic system continuously produced formate during the light-dark cycles, and a quantum yield of 1.85  
35 ± 0.29% was finally achieved (Figure 4d). These findings thus provide strong evidence for the good promise of  
36 MHPs in solar-to-chemical conversion by integrating their superior optoelectronic properties with the  
37 biosynthetic pathways in nature.  
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## 54 Conclusion

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5 In conclusion, we have demonstrated the long-lived charges and the accompanying persistent luminescence in  
6 MHPs. DFT calculations confirm that the point and Schottky defects in the nanocrystals supply abundant  
7 occupied states near the CBM, and the persistent luminescence in MHPs is produced with the cascade upward  
8 depletion mechanism. An MHPs-based light-driven biosynthetic system was further constructed for the  
9 production of fine chemicals from CO<sub>2</sub> by integrating the superior optoelectronic properties of MHPs with the  
10 CO<sub>2</sub>-processing capability of enzymes. This investigation demonstrates the generation of long-lived charges in  
11 MHP nanocrystals, and also offers an opportunity for developing light-driven biosynthetic systems to produce  
12 high-value chemicals with solar energy. Moreover, beyond the development of advanced solar-to-chemical  
13 synthesis systems, the defects-associated long-lived charges establish further avenues for applications of MHPs  
14 in artificial photosynthesis and renewable solar fuels production.  
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## 26 27 **Supporting Information**

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29 Supporting Information is available and includes TEM images of the nanoparticles, photos of the MHP  
30 nanoparticle dispersions, XRD analysis of the MHP nanoparticles, absorption and photoluminescence spectra  
31 (solid line) of the MHP nanoparticles, persistent luminescence decay images of the MHP nanoparticles, XPS  
32 analysis of the p-CsPbBr<sub>3</sub> nanocrystals, synthesis procedure of the Rh-based electron shuttle M, the electron  
33 transfer process in the light-driven biosynthetic system, photocurrent analysis of the nanoparticles, the light-  
34 driven NADH and formate generation under different conditions.  
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## 43 **Conflict of Interest**

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46 The authors declare no competing interests.  
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## 50 **Acknowledgments**

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