

Direct Partial Transformation of 2D Antimony Oxybromide to Halide Perovskite Heterostructure for Efficient CO₂ Photoreduction

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The photocatalytic activity of lead-free perovskite heterostructures currently suffers from low efficiency due to the lack of active sites and the inadequate photogenerated carrier separation, the latter of which is hindered by slow charge transfer at the heterostructure interfaces. Herein, a facile strategy is reported for the construction of lead-free halide-perovskite-based heterostructure with swift interfacial charge transfer, achieved through direct partial conversion of 2D antimony oxybromide Sb₄O₅Br₂ to generate Cs₃Sb₂Br₉/Sb₄O₅Br₂ heterostructure. Compared to the traditional electrostatic self-assembly method, this approach endows the Cs₃Sb₂Br₉/Sb₄O₅Br₂ heterostructure with a tightly interconnected interface through in situ partial conversion, significantly accelerating interfacial charge transfer and thereby enhancing the separation efficiency of photogenerated carriers. The cobalt-doped Cs₃Sb₂Br₉/Sb₄O₅Br₂ heterostructure demonstrates a record-high electron consumption rate of 840 μmol g⁻¹ h⁻¹ for photocatalytic CO₂ reduction to CO coupled with H₂O oxidation to O₂, which is over 74- and 16-fold higher than that of individual Sb₄O₅Br₂ and Cs₃Sb₂Br₉, respectively. This work provides an effective strategy for promoting charge separation in photocatalysts to improve the performance of artificial photosynthesis.

diverse photocatalysts.^[3] Consequently, halide perovskite materials, which have recently gained prominence in the optoelectronic device domains,^[4] have garnered significant attention in the field of photocatalytic CO₂ reduction,^[5] owing to their desirable attributes, including outstanding visible light absorption capacity and prolonged carrier lifetime.^[6] In particular, Sb-based perovskites exhibit reduced toxicity than Pb-based perovskites, while also demonstrating superior light absorption coefficients and extended carrier lifetimes compared to other lead-free halide perovskites (e.g., Sn-based, Bi-based, AgBi-based, etc.).^[7] Therefore, they are viewed as promising candidates for photocatalytic CO₂ reduction.^[8]

Nonetheless, akin to Pb-based perovskites, isolated Sb-based perovskite nanomaterials also encounter a shortage of high-activity sites. Furthermore, their nanosecond-scale photogenerated carrier lifetimes fall short of efficiently catalyzing the sluggish reactions of CO₂ reduction and water oxidation. Therefore, the

photocatalytic activity of standalone Sb-based perovskite nanomaterials for CO₂ reduction is also very low. Constructing ligand-free Sb-based perovskite nanomaterials has been demonstrated to be an effective solution to facilitate the exposure of active sites and strengthen CO₂ adsorption, bringing forth enhanced performance for photocatalytic CO₂ reduction.^[9] The charge separation efficiency can be enhanced by introducing mixed halides, which can not only tune the band gap of Sb-based perovskites,^[10] but also promote favorable charge redistribution due to lower octahedral distortion, resulting in strengthened CO₂ adsorption and activation.^[11] Another widely adopted and proven effective approach to facilitating charge separation is the construction of heterostructures. For instance, depositing Sb-based perovskite onto Co₃O₄ or Bi₂MoO₆ can boost its charge separation, ultimately enhancing its photocatalytic performance.^[12] However, the current primary methods for constructing Sb-based perovskite heterostructures encompass physical mixing and in situ deposition, and the resultant loose interfaces impede the process of interfacial charge transfer, ultimately constraining the efficient separation of photogenerated carriers. Therefore, the development of

1. Introduction

Mimicking natural photosynthesis to convert CO₂ and H₂O into value-added chemicals with renewable solar energy is an appealing approach to mitigating the energy and climate issues due to the excessive combustion of fossil fuels.^[1] In this technology, the light absorption efficiency and charge separation efficiency are pivotal in determining the performance of photocatalytic CO₂ reduction,^[2] serving as the cornerstone for the development of

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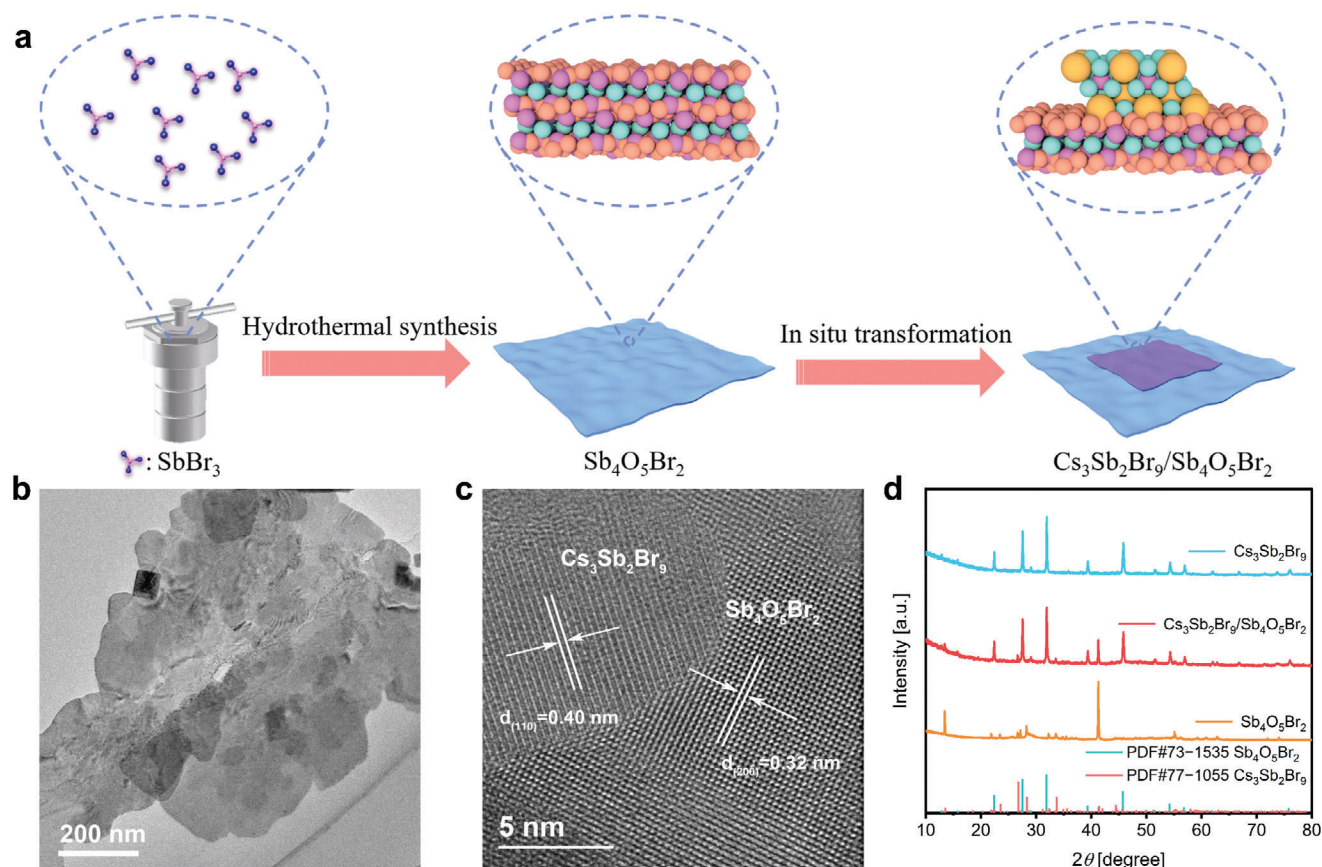


Figure 1. a) Schematic diagram of $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ preparation process. b,c) TEM and HRTEM images of $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$. d) XRD patterns of $\text{Cs}_3\text{Sb}_2\text{Br}_9$, $\text{Sb}_4\text{O}_5\text{Br}_2$ and $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$.

Sb-based perovskite heterostructures with tightly contacted interfaces is essential to enhance their performance for CO_2 photoreduction.

Herein, we reported a facile self-templating method for constructing Sb-based perovskite heterostructures with intimate interfacial contact. Specifically, for the first time, 2D $\text{Sb}_4\text{O}_5\text{Br}_2$ nanosheets were successfully synthesized via a hydrothermal method and employed as templates to generate 2D/2D $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ heterostructures through direct partial conversion. Our strategy primarily rests on the following crucial considerations. First, 2D nanosheets offer abundant active sites and shorter carrier transfer distances to the surface, facilitating the adsorption and activation of the reaction substrates.^[13] Second, the large interface contact area of the 2D/2D heterostructure can promote interfacial charge transfer and separation.^[14] Third, in situ direct conversion can form a tightly contacting interface, thereby accelerating interfacial charge transfer and separation. As anticipated, the prepared $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ heterostructure exhibits significantly improved interfacial photo-generated carrier separation compared to the heterostructure prepared by the traditional electrostatic self-assembly method. Through cobalt ion doping to enhance active sites, the fabricated $\text{Co}@\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ heterostructure can attain an electron consumption rate of $840 \mu\text{mol g}^{-1} \text{h}^{-1}$ for photocatalytic CO_2 reduction to CO without the necessity of any organic sacrificial

agents, surpassing the performances of other halide perovskite materials reported under comparable conditions (Table S1, Supporting Information).

2. Results and Discussion

2.1. Preparation and Characterization of 2D/2D $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ Heterostructures

The synthesis process of the $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ heterostructure is illustrated in Figure 1a, and detailed synthetic steps are described in the Experimental Section. Briefly, $\text{Sb}_4\text{O}_5\text{Br}_2$ nanosheets were first synthesized by a hydrothermal method and subsequently dispersed uniformly in a solution of isopropanol containing saturated CsBr. Under vigorous stirring, a certain amount of HBr was added to trigger the in situ transformation from $\text{Sb}_4\text{O}_5\text{Br}_2$ to $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$. During this process, HBr can effectively drive Sb^{3+} and Br^- ions to release from the lattice of $\text{Sb}_4\text{O}_5\text{Br}_2$ nanosheets to their surfaces, thereby enabling the in situ recrystallization with Cs^+ ions in the solution to form $\text{Cs}_3\text{Sb}_2\text{Br}_9$ nanosheets ($\text{Sb}_4\text{O}_5\text{Br}_2 + \text{HBr} + \text{CsBr} \rightarrow \text{Cs}_3\text{Sb}_2\text{Br}_9 + \text{H}_2\text{O}$). Simultaneously, the proportion of the two components in the $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ heterostructure can also be effectively regulated by controlling the amount of HBr. For comparison, $\text{Cs}_3\text{Sb}_2\text{Br}_9:\text{Sb}_4\text{O}_5\text{Br}_2$ composites were additionally

prepared by integrating $\text{Cs}_3\text{Sb}_2\text{Br}_9$ and $\text{Sb}_4\text{O}_5\text{Br}_2$ via the conventional electrostatic self-assembly method, with comprehensive details outlined in the Experimental Section.

The morphologies of the as prepared heterostructures were analyzed using transmission electron microscopy (TEM) and atomic force microscopy (AFM). As illustrated in Figure S1a (Supporting Information), TEM measurement revealed that the prepared $\text{Sb}_4\text{O}_5\text{Br}_2$ templates exhibit an irregular nanosheet morphology. The high-resolution TEM (HRTEM) image of $\text{Sb}_4\text{O}_5\text{Br}_2$ displays a lattice spacing of 0.32 nm, corresponding to the (200) plane of monoclinic $\text{Sb}_4\text{O}_5\text{Br}_2$ (Figure S1b, Supporting Information). Additionally, AFM measurement confirmed the nanosheet morphology of $\text{Sb}_4\text{O}_5\text{Br}_2$, with an average thickness of approximately 10 nm (Figure S2, Supporting Information). Figure 1b displays the TEM image of the $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ heterostructure formed by in situ transformation, where it is clearly visible that small and darker nanosheets with a diameter of approximately 40 nm are distributed on the surface of the $\text{Sb}_4\text{O}_5\text{Br}_2$ nanosheets. Further, corresponding HRTEM measurements demonstrated two distinct lattice spacings of 0.32 and 0.40 nm, which can be attributed to the (200) plane of $\text{Sb}_4\text{O}_5\text{Br}_2$ and the (110) plane of $\text{Cs}_3\text{Sb}_2\text{Br}_9$, respectively (Figure 1c). These lattice spacings are consistent with those of pure $\text{Sb}_4\text{O}_5\text{Br}_2$ and $\text{Cs}_3\text{Sb}_2\text{Br}_9$, as shown in Figures S1, S3 (Supporting Information), respectively. Energy-dispersive X-ray spectroscopy (EDS) mapping measurements were further conducted to investigate the elemental distribution in the $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ heterostructure. As depicted in Figure S4 (Supporting Information), Sb and O are uniformly dispersed throughout the sample, while Cs and Br are relatively concentrated. The above results provide preliminary evidence for the successful preparation of the $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ heterostructure.

Powder X-ray diffraction (PXRD) measurements were conducted to delve deeper into the crystal structure characteristics of the $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ heterostructure. As presented in Figure 1d, the as-prepared $\text{Sb}_4\text{O}_5\text{Br}_2$ nanosheets exhibit sharp diffraction peaks, indicating high crystallinity. These diffraction peaks are situated at 13.5° , 21.9° , 27.3° , 28.4° , and 41.4° , corresponding to the (100), (012), (200), (-104), and (300) planes of the monoclinic phase $\text{Sb}_4\text{O}_5\text{Br}_2$ (JCPDS No. 73–1535). After undergoing in situ partial conversion, the characteristic diffraction peaks of $\text{Sb}_4\text{O}_5\text{Br}_2$ are still observable in the sample. More notably, the emergence of characteristic diffraction peaks corresponding to the highly crystalline hexagonal phase $\text{Cs}_3\text{Sb}_2\text{Br}_9$ (JCPDS No. 77–1055) provides compelling evidence for the successful preparation of the $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ heterostructure.^[15]

Fourier transform infrared (FTIR) spectroscopy and Raman spectroscopy measurements further confirmed the successful preparation of the $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ composites. As shown in Figure S5 (Supporting Information), $\text{Sb}_4\text{O}_5\text{Br}_2$ exhibits a prominent vibration peak of Sb–O–Sb at 826 cm^{-1} , with characteristic peaks at 703 and 494 cm^{-1} attributed to the stretching and bending vibrations of the Sb–O bond, respectively.^[16] In contrast, $\text{Cs}_3\text{Sb}_2\text{Br}_9$, due to its inherent ionic crystalline nature, does not exhibit significant characteristic signals in the FTIR spectrum. Notably, in the $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ heterostructure, the aforementioned characteristic peaks of $\text{Sb}_4\text{O}_5\text{Br}_2$ can be distinctly detected, which strongly supports the notion that the compos-

ite is constructed through partial conversion using $\text{Sb}_4\text{O}_5\text{Br}_2$ as the substrate. Moreover, the Raman signals can be unequivocally observed belonging to $\text{Cs}_3\text{Sb}_2\text{Br}_9$ (72 , 183 , and 213 cm^{-1} corresponding to E_g and A_{1g} modes)^[17] and $\text{Sb}_4\text{O}_5\text{Br}_2$ (104 , 124 , and 170 cm^{-1} are observed to the external Sb–Br stretching pattern of A_{1g} and E_g). The peak observed at 261 cm^{-1} is from the vibration of O–Sb–O, and the 461 cm^{-1} band generated by oxygen atoms motion is B_{1g})^[18] in $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ heterostructure (Figure S6, Supporting Information). These results collectively demonstrate the successful preparation of the $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ heterostructure.

2.2. Interfacial Charge Transfer Dynamics of $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ Heterostructures

The UV–visible diffuse reflectance spectroscopy (UV–vis DRS) and ultraviolet photoelectron spectroscopy (UPS) measurements were employed to assess the thermodynamic feasibility of the composites for the photocatalytic CO_2 reduction. As depicted in Figure 2a, $\text{Sb}_4\text{O}_5\text{Br}_2$ exhibits relatively weak absorption in the visible light region, with an absorption edge at only 411 nm . In contrast, $\text{Cs}_3\text{Sb}_2\text{Br}_9$ demonstrates superior light absorption capability in the UV–vis region below 501 nm . Notably, the characteristic absorption features of both $\text{Sb}_4\text{O}_5\text{Br}_2$ and $\text{Cs}_3\text{Sb}_2\text{Br}_9$ can be observed in the $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ heterostructure, further confirming the successful synthesis of the composite material. According to the corresponding Tauc plots (Figure S7, Supporting Information), the optical band gaps of $\text{Cs}_3\text{Sb}_2\text{Br}_9$ and $\text{Sb}_4\text{O}_5\text{Br}_2$ can be determined to be 2.54 and 2.67 eV , respectively, which are consistent with previous reports.^[19] Figures 2b and c display the UPS spectra of $\text{Cs}_3\text{Sb}_2\text{Br}_9$ and $\text{Sb}_4\text{O}_5\text{Br}_2$, respectively. From these spectra, the valence band edge potentials (E_{VB}) of $\text{Cs}_3\text{Sb}_2\text{Br}_9$ and $\text{Sb}_4\text{O}_5\text{Br}_2$ are calculated to be 2.08 and 2.02 V versus the standard hydrogen electrode (SHE), respectively. By combining the values of E_g and E_{VB} , the conduction band edge potentials (E_{CB}) of $\text{Cs}_3\text{Sb}_2\text{Br}_9$ and $\text{Sb}_4\text{O}_5\text{Br}_2$ can be inferred to be -0.46 and -0.65 V versus SHE, respectively. In addition, Mott–Schottky measurements were conducted to determine the flat-band potentials of $\text{Cs}_3\text{Sb}_2\text{Br}_9$ and $\text{Sb}_4\text{O}_5\text{Br}_2$, which were found to be -0.46 and -0.65 V versus SHE, respectively, aligning with the UPS measurement results (Figure S8, Supporting Information). Notably, staggered energy band alignments exist in the $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ composite, which is advantageous for the separation and transfer of photogenerated carriers. Furthermore, the migration direction of photogenerated carriers in the $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ heterostructure during the photocatalytic process was investigated by the in situ photo-excited high-resolution X-ray photoelectron spectroscopy (XPS). As presented in Figures 2d and e, under illumination, the binding energy of O 1s in $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ shifts toward higher binding energy (0.22 – 0.49 eV), while the binding energy of Cs 3d shifts toward lower binding energy (0.41 eV). These changes indicate that light irradiation causes the electron densities of around the Cs and O atoms to increase and decrease, respectively, signifying that the photogenerated carriers undergo directional transfer at the heterojunction interface. Specifically, photogenerated electrons transfer from $\text{Sb}_4\text{O}_5\text{Br}_2$ to $\text{Cs}_3\text{Sb}_2\text{Br}_9$, while photogenerated holes transfer in the opposite direction. The band structure

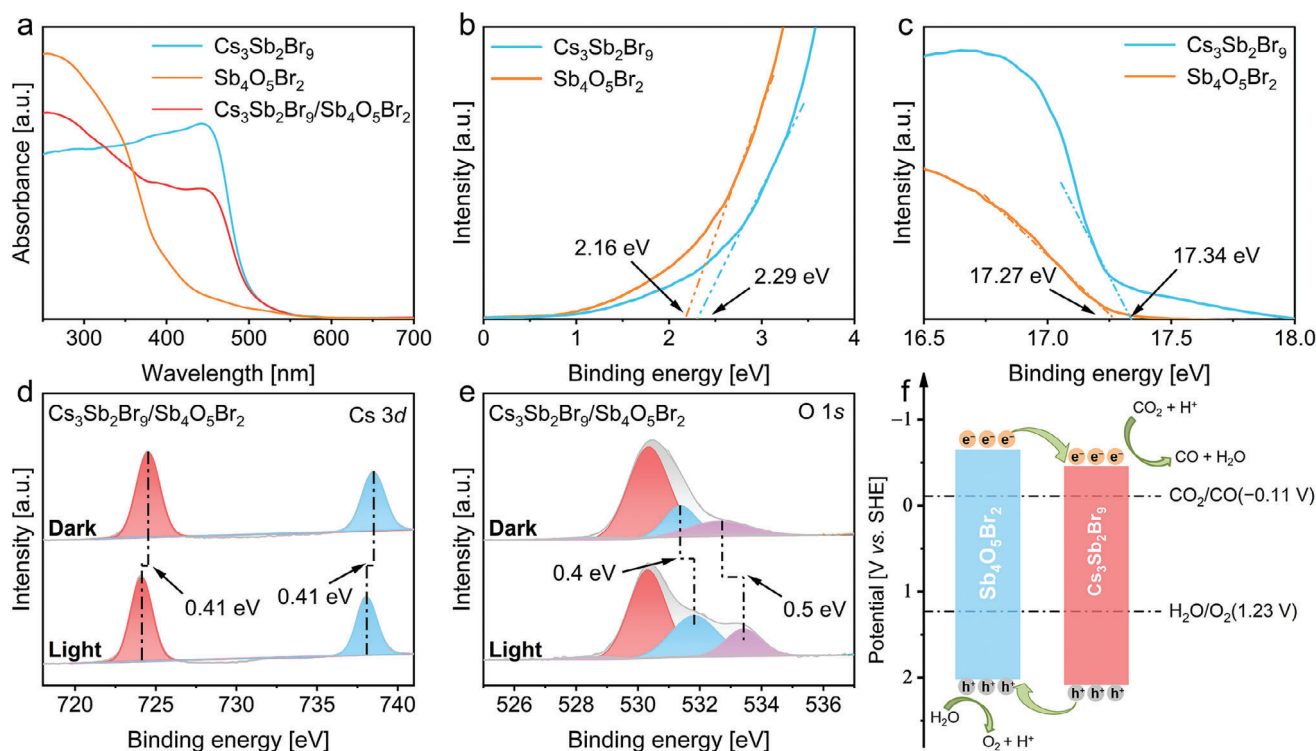


Figure 2. a) UV-vis DRS spectra of $\text{Cs}_3\text{Sb}_2\text{Br}_9$, $\text{Sb}_4\text{O}_5\text{Br}_2$, and $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$. b, c) UPS spectra of $\text{Cs}_3\text{Sb}_2\text{Br}_9$ and $\text{Sb}_4\text{O}_5\text{Br}_2$. In situ high-resolution XPS spectra of $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ under the light and dark conditions: d) Cs 3d and e) O 1s. f) Band structure diagram of $\text{Cs}_3\text{Sb}_2\text{Br}_9$ and $\text{Sb}_4\text{O}_5\text{Br}_2$.

and electron transfer direction of the $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ heterostructure are schematically illustrated in Figure 2f.

The dynamics of photogenerated carriers in photocatalysts is a crucial factor determining their photocatalytic performance.^[20] Therefore, the dynamics of photogenerated carriers in the $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ heterostructure were further investigated through steady-state and transient photoluminescence (PL) measurements. The excitation wavelength of 420 nm was chosen to avoid the absorption of $\text{Sb}_4\text{O}_5\text{Br}_2$. As depicted in Figure 3a, pure $\text{Cs}_3\text{Sb}_2\text{Br}_9$ exhibits strong PL emission with a characteristic peak at 490 nm. There is an insignificant reduced PL intensity in the $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ composite based on the electrostatic self-assembly method, indicating the sluggish electron transfer between $\text{Cs}_3\text{Sb}_2\text{Br}_9$ and $\text{Sb}_4\text{O}_5\text{Br}_2$ because of the structural separation of the two components. It is worth noting that the $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ heterostructure exhibits dramatic PL quenching, indicating that the high-quality interface is beneficial for the separation of photogenerated carriers. The time-resolved PL (TRPL) measurements further confirmed that the heterostructure formed by in situ conversion promotes interfacial charge separation, as shown in Figure 3b. The TRPL decay curve of pure $\text{Cs}_3\text{Sb}_2\text{Br}_9$ represents both radiative and non-radiative pathways of photogenerated excitons in $\text{Cs}_3\text{Sb}_2\text{Br}_9$. The average PL lifetime of $\text{Cs}_3\text{Sb}_2\text{Br}_9$ can be calculated by fitting the corresponding TRPL decay curve with a multi-exponential function, resulting in a value of 3.30 ns (Table S2, Supporting Information). In comparison to $\text{Cs}_3\text{Sb}_2\text{Br}_9$, the $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ composite exhibits accelerated PL decay with a shorter average PL lifetime of 2.07 ns, further indicating that interfacial charge

transfer occurs between $\text{Cs}_3\text{Sb}_2\text{Br}_9$ and $\text{Sb}_4\text{O}_5\text{Br}_2$. In contrast, the PL decay in the $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ heterostructure is significantly accelerated, and the average lifetime is shortened to 1.37 ns, indicating that the rapid charge transfer at the interface of the $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ heterostructure. These results also confirm that the closely contacting interface is highly beneficial for the separation of photogenerated charge carriers. Photocurrent response ($I-t$) and electrochemical impedance spectroscopy (EIS) measurements further demonstrated the advantage of the in situ transformation strategy for accelerating interfacial charge transport and separation. As shown in Figure 3c, the photocurrent densities of the $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ were apparently higher than those of single $\text{Cs}_3\text{Sb}_2\text{Br}_9$, $\text{Sb}_4\text{O}_5\text{Br}_2$ and the $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ heterostructure formed by electrostatic self-assembly. In addition, the diameter of the Nyquist semi-circle of the $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ heterostructure is also significantly smaller than that of the $\text{Cs}_3\text{Sb}_2\text{Br}_9$, $\text{Sb}_4\text{O}_5\text{Br}_2$ and $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$, respectively (Figure S9, Supporting Information).

The surface photovoltage (SPV) measurements were further carried out to confirm the favorable effects of the heterostructure formed by in situ conversion strategy on photogenerated carrier transport and separation. The AFM height mapping images reveal that both the pristine $\text{Sb}_4\text{O}_5\text{Br}_2$ and the transformed $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ exhibit a nanosheet morphology. The Kelvin probe force microscopy (KPFM) images (Figures S10, S11, Supporting Information) and the SPV difference are shown in Figure 3d. Under illumination, the larger change in the SPV signal typically indicates more accumulation

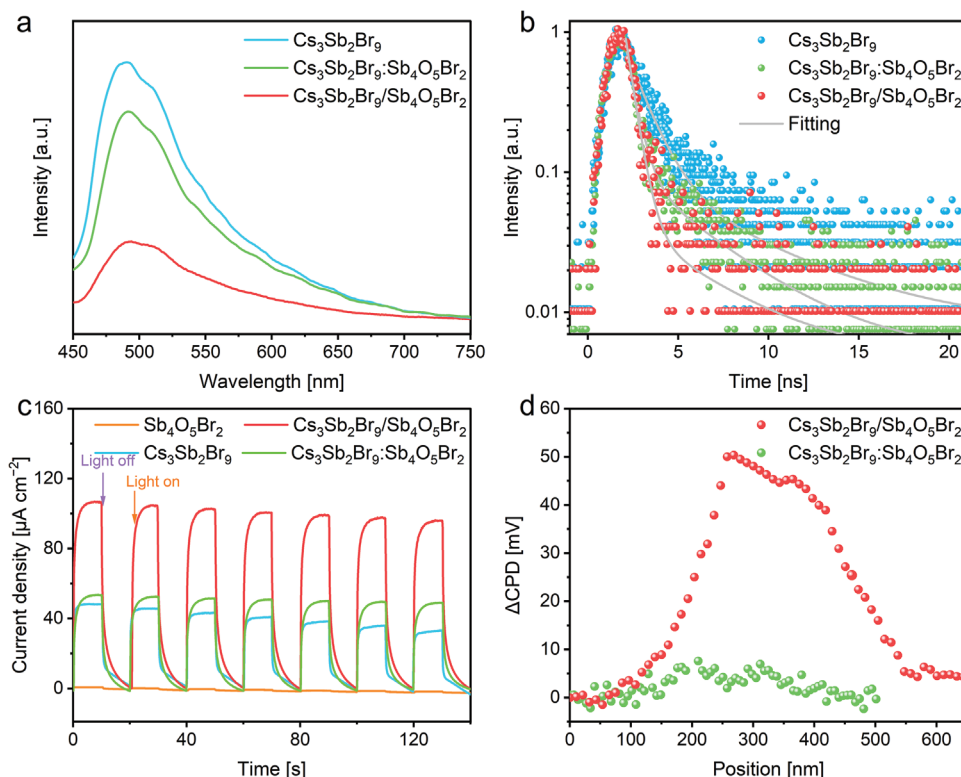


Figure 3. a) Steady-state PL and b) time-resolved PL decay traces of $\text{Cs}_3\text{Sb}_2\text{Br}_9$, $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ and $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$. c) $I-t$ curves of $\text{Cs}_3\text{Sb}_2\text{Br}_9$, $\text{Sb}_4\text{O}_5\text{Br}_2$, $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$, and $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$. d) Surface potential changes of $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ and $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ by subtracting the potential under dark conditions from that under illumination.

of photogenerated charge on the surface of semiconductor. Pure $\text{Sb}_4\text{O}_5\text{Br}_2$ has a negligible SPV response under light irradiation, due to the rapid charge carrier recombination and the weak light absorption capacity (Figure S12, Supporting Information). In addition, the SPV response of pure $\text{Cs}_3\text{Sb}_2\text{Br}_9$ is correspondingly negligible (Figure S13, Supporting Information). Notably, as shown in Figure 3d, $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ shows an obvious change of SPV signals, which is also substantially larger than that of $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ composite. Apparently, the $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ heterostructure with a close contact interface can promote interfacial charge separation, resulting in a high concentration of photogenerated charge carriers at the semiconductor surface. The significant difference in SPV signals furnishes strong evidence for the accumulation and consumption of space charge on the interface of the $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ heterostructure interface.

2.3. Photocatalytic CO_2 Reduction Activity and Mechanism of $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ Heterostructures

The photocatalytic CO_2 reduction activities of all the prepared samples were evaluated using a gas–solid reaction system with the presence of H_2O vapor. A 300 W Xe lamp with a light intensity of 100 mW cm^{-2} was used to simulate sunlight. The gaseous products were analyzed by gas chromatography, and neither CH_4 nor H_2 were detected, revealing that CO was the primary product of CO_2 reduction for all the evaluated samples

(Figure S14, Supporting Information). The corresponding CO generation rates of all photocatalysts are shown in Figure 4a. The $\text{Sb}_4\text{O}_5\text{Br}_2$ nanosheets exhibit very inferior activity for photocatalytic CO_2 reduction with a CO production rate of $6 \mu\text{mol g}^{-1} \text{ h}^{-1}$. This is attributed to their weak light absorption capacity and weak thermodynamic driving force for the reduction reaction. Meanwhile, individual $\text{Cs}_3\text{Sb}_2\text{Br}_9$ also displays low activity for photocatalytic CO_2 reduction ($26 \mu\text{mol g}^{-1} \text{ h}^{-1}$), despite its ideal light absorption and energy band structure, primarily due to its deficiency active sites and insufficient photogenerated carriers. Compared with $\text{Cs}_3\text{Sb}_2\text{Br}_9$ and $\text{Sb}_4\text{O}_5\text{Br}_2$, the CO_2 reduction capacity of the $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ catalyst formed by electrostatic self-assembly was slightly improved with a CO generation rate of $41 \mu\text{mol g}^{-1} \text{ h}^{-1}$. This result should be attributed to the large distance between the two composites formed by electrostatic self-assembly, which hinders the charge transfer and leads to insufficient photogenerated carrier separation. For $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$, the proportion of $\text{Cs}_3\text{Sb}_2\text{Br}_9$ and $\text{Sb}_4\text{O}_5\text{Br}_2$ was optimized via controlling the HBr volume (Figure S15, Supporting Information). Notably, the optimal $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ delivered significantly improved photocatalytic CO_2 reduction activity, and the CO yield is as high as $202 \mu\text{mol g}^{-1} \text{ h}^{-1}$, which suggests that the close-contact heterostructure interface is conducive to improving the photogenerated carrier separation efficiency. Moreover, considering that incorporating active metal ions into halide perovskites can enhance the catalytic activity for CO_2 reduction by increasing catalytic site and improving charge separation

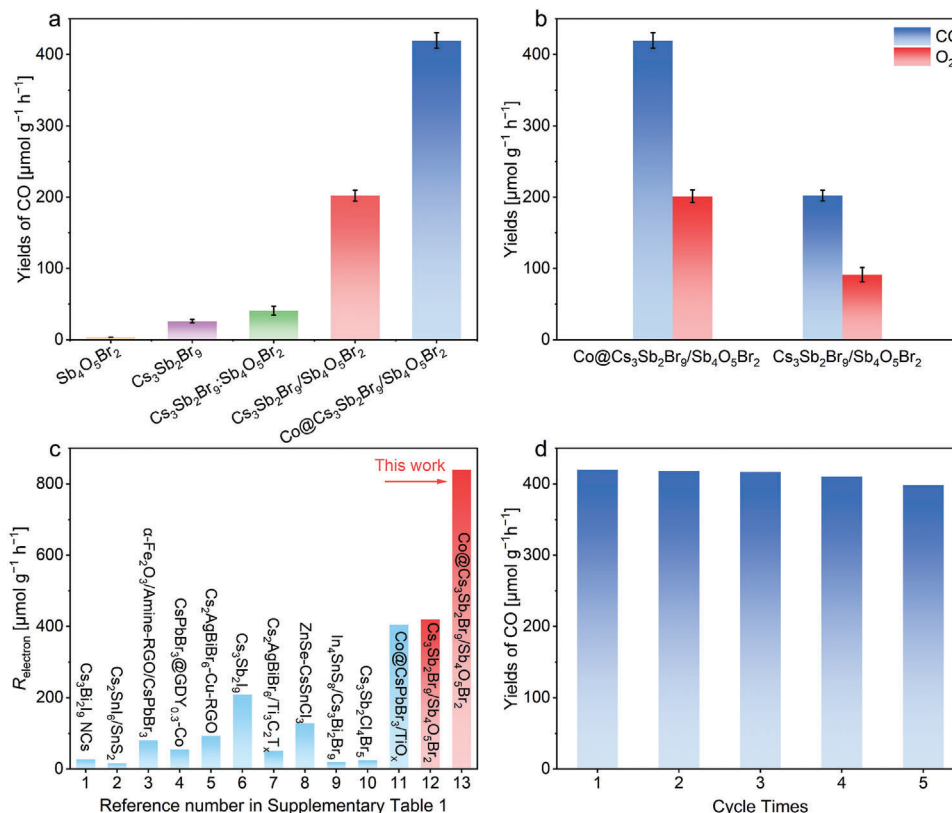


Figure 4. a) Yields of CO with different catalysts. b) Yields of reduced and oxidized products with $\text{Co@Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ and $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ as photocatalysts. c) Comparison of electron consumption rates of reported halide perovskite-based photocatalysts. d) Yields of CO for consecutive five cycles with 2 h each using $\text{Co@Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ as photocatalyst.

efficiency, a cobalt doped $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ heterostructure, designated as $\text{Co@Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$, was also synthesized (Figures S16–S18, Supporting Information). The CO formation rate of $\text{Co@Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ could reach up to $420 \mu\text{mol g}^{-1} \text{h}^{-1}$, which is more than an order of magnitude higher than that of $\text{Cs}_3\text{Sb}_2\text{Br}_9$ and $\text{Sb}_4\text{O}_5\text{Br}_2$ and $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ composites alone (Figure 4a and Figure S19, Supporting Information). Meanwhile, the oxidation products O_2 of $\text{Co@Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ and $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ were quantified, averaging 202 and $91 \mu\text{mol g}^{-1} \text{h}^{-1}$, respectively, maintaining a nearly stoichiometric of 1:2 ratio with respect to the yield of CO (Figure 4b). The corresponding electron consumption rate (R_{electron}) of $\text{Co@Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ can reach up to $840 \mu\text{mol g}^{-1} \text{h}^{-1}$, which is much higher than that of reported halide-perovskite-based photocatalysts, as shown in Figure 4c. The apparent quantum efficiencies (AQEs) for $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$, $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$, and $\text{Co@Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ were evaluated under 365 and 425 nm incident light (Table S3, Supporting Information). The $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ only displays low AQE values of 0.02% and 0.01% under 365 and 425 nm LEDs, respectively. In sharp contrast, $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ delivered significantly higher AQE values of 0.11% and 0.08% under identical conditions, suggesting the facilitated charge transfer benefitting from the direct partial conversion strategy. Moreover, the AQE values of $\text{Co@Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ were further increased, demonstrating improved photon conversion after cobalt doping.

In addition, the photocatalytic stability of $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ and $\text{Co@Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ were estimated by cyclic experiments. As shown in Figure 4d and Figure S20 (Supporting Information), the CO generation rate decreased by less than 10% after 5 cycles, indicating that $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ and $\text{Co@Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ have good stability in the gas-solid reaction system. Further, XRD and XPS measurements confirmed that the crystal structure and chemical state of $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ remained well after the photocatalytic reaction (Figures S21, S22, Supporting Information).

Using $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ as photocatalyst, further controlled experiments were conducted to determine the sources of CO and O_2 . As shown in Figure S23 (Supporting Information), no products were detected in the absence of light or catalyst, indicating that the CO_2 reduction reaction was triggered by light irradiation on the catalyst. In addition, a control experiment that was conducted in the absence of water vapor or with the replacement of CO_2 with Ar also demonstrated negligible generation of CO, indicating that CO originates from CO_2 photoreduction and the electron source for this photoreduction comes from water oxidation. Furthermore, the origins of the products were further verified by isotopic labeling experiments with $^{13}\text{CO}_2$ and H_2^{18}O as feedstocks. As presented in Figure S24 (Supporting Information), the results of mass spectrometry analysis from the $^{13}\text{CO}_2$ isotope tracing experiment reveal an obvious signal at $m/z = 29$, which belongs to ^{13}CO , proving that the CO originates from

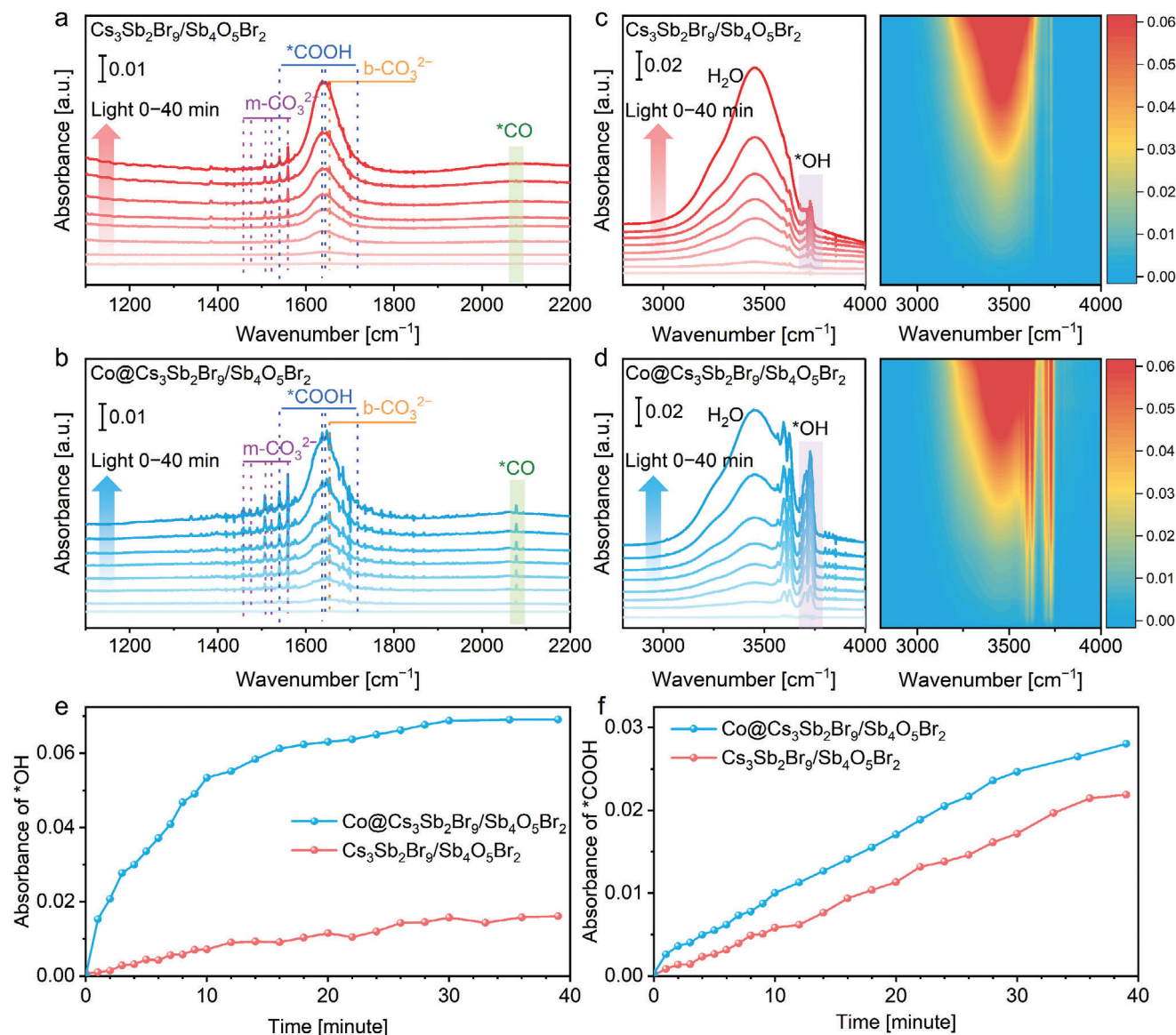


Figure 5. a,c) In situ FTIR spectra for photocatalytic CO₂ conversion over Cs₃Sb₂Br₉/Sb₄O₅Br₂. b,d) In situ FTIR spectra for photocatalytic CO₂ conversion over Co@Cs₃Sb₂Br₉/Sb₄O₅Br₂. e) Plots of time against adsorption strength in the *COOH adsorption mode in in situ FTIR spectra. f) Plots of time against adsorption strength in the water stretching mode in in situ FTIR spectra.

CO₂ photoreduction. Additionally, in the H₂¹⁸O isotope tracing experiment, the obvious signal at $m/z = 36$ corresponding to ¹⁸O₂ can be detected, confirming that O₂ was derived from water oxidation.^[21]

The role of doped cobalt in steering the dynamics of photogenerated charge carriers was also investigated. As shown in Figure S25 (Supporting Information), the PL intensity of Co@Cs₃Sb₂Br₉/Sb₄O₅Br₂ drastically decreased in comparison with that for Cs₃Sb₂Br₉/Sb₄O₅Br₂, indicating the improved separation of photogenerated carriers by doped Co ions. In addition, the PL decay in the Co@Cs₃Sb₂Br₉/Sb₄O₅Br₂ was accelerated, and the average lifetime was shortened from 1.37 to 0.84 ns, suggesting the facilitated charge transfer (Figure S26 and Table S2, Supporting Information). The favored charge

carrier separation and migration by cobalt doping were further validated by the higher photocurrent densities and smaller Nyquist semicircle of Co@Cs₃Sb₂Br₉/Sb₄O₅Br₂ compared to those of Cs₃Sb₂Br₉/Sb₄O₅Br₂ (Figures S27,S28, Supporting Information).

Furthermore, the adsorption and activation mechanisms of CO₂ and H₂O during the photoconversion process were analyzed using in situ FTIR measurement. The measurements were conducted under equilibrium adsorption of CO₂-containing water vapor. As illustrated in Figure 5a,b, with the increase in illumination time, the emergence of new characteristic peaks of 1618, 1636, 1647, and 1716 cm⁻¹ were observed for both Cs₃Sb₂Br₉/Sb₄O₅Br₂ and Co@Cs₃Sb₂Br₉/Sb₄O₅Br₂. These peaks were assigned to the *COOH group,^[20] which is

generally considered to be important intermediates in the CO₂ reduction process.^[22] In addition, the peaks at 1317, 1458, 1473, 1507, 1549 and 1559 cm⁻¹ can be attributed to monodentate carbonate (m-CO₃²⁻), while the bidentate carbonate (b-CO₃²⁻) peaks were observed at 1363 and 1653 cm⁻¹. The observation of infrared peaks at 1696 cm⁻¹ was attributed to the *CO.^[23] Comparatively, for Co@Cs₃Sb₂Br₉/Sb₄O₅Br₂, the intensity of characteristic peaks (*COOH and *CO) was significantly higher, indicating that Co doping is conducive to the formation of *COOH and *CO (Figure 5b). The peak at 3200–3800 cm⁻¹ is assigned to adsorbed H₂O molecules,^[24] confirming that H₂O molecules are involved in the CO₂ reduction process, and the intensity of these peaks is commonly used to represent the ability of water activation.^[25] The peak at 3300 cm⁻¹ is associated with the stretching vibration of hydroxyl groups, typically indicating physically adsorbed H₂O molecules. The characteristic peak in the range of 3500–3800 cm⁻¹ generally represents the interaction between metal and hydroxyl groups (Sb–OH).^[26] In contrast, the metal hydroxyl peak of the Co@Cs₃Sb₂Br₉/Sb₄O₅Br₂ composite within the wavenumber range of 3700–3727 cm⁻¹ demonstrates a significant enhancement effect, which robustly indicates a substantial improvement in its water activation capability (as shown in Figure 5c,d). Furthermore, a meticulous analysis of the trend in *OH signal intensity over time reveals that in the Cs₃Sb₂Br₉/Sb₄O₅Br₂ system, the Sb–OH content gradually and steadily increases to an equilibrium state within the 0 to 40 min period. Concurrently, the Sb–OH on the surface of Co@Cs₃Sb₂Br₉/Sb₄O₅Br₂ rapidly accumulates to its equilibrium level within the initial 10 min, and its Sb–OH concentration at equilibrium is over 3.5 times higher compared to that of the Cs₃Sb₂Br₉/Sb₄O₅Br₂ material. Additionally, the evolution rate of the *COOH intermediate on Co@Cs₃Sb₂Br₉/Sb₄O₅Br₂ is faster than that based on Cs₃Sb₂Br₉/Sb₄O₅Br₂. This result clearly demonstrates that the incorporation of Co significantly promotes the water activation process, optimizes the carrier separation efficiency of the heterojunction, and thereby contributes to enhancing the CO₂ reduction efficiency (as shown in Figure 5e,f). Furthermore, the linear sweep voltammetry (LSV) curves for CO₂ reduction and oxygen evolution reaction (OER) provide additional evidence that cobalt doping facilitates both CO₂ reduction and H₂O oxidation (Figures S29,S30, Supporting Information), which is consistent with the results obtained from in situ infrared spectroscopy.

Based on these results, we can propose the reaction pathway of Cs₃Sb₂Br₉/Sb₄O₅Br₂ photocatalytic CO₂ reduction coupled with water oxidation. As illustrated in Figure S31 (Supporting Information), first, Cs₃Sb₂Br₉/Sb₄O₅Br₂ absorbs photons and produces electron-hole pairs. Subsequently, effective charge separation occurs for the photogenerated carriers, with electrons flowing toward Cs₃Sb₂Br₉ and holes accumulating in Sb₄O₅Br₂. Following this, the photogenerated electrons in the conduction band of Cs₃Sb₂Br₉ initiate the reduction reaction of CO₂ through a proton-coupled electron transfer pathway, forming intermediates such as *COOH and *CO during the process. These intermediates then undergo further proton-coupled electron transfer reactions to produce CO. Simultaneously, the photogenerated holes in the valence band of Sb₄O₅Br₂ engage in the oxidation of H₂O to *OH intermediates, ultimately leading to the production O₂.

3. Conclusion

In summary, two 2D/2D lead-free halide-perovskite-based heterostructures of Sb₄O₅Br₂/Sb₄O₅Br₂ and Co@Cs₃Sb₂Br₉/Sb₄O₅Br₂ have been successfully prepared by combining self-templating method with direct partial conversion approach and served as photocatalysts for CO₂ reduction coupled with water oxidation. This in situ partial transformation technology results in the formation of a tightly interconnected interface between Cs₃Sb₂Br₉ and Sb₄O₅Br₂, which can accelerate interfacial photogenerated carrier separation, as demonstrated by a combination of steady-state and transient photoluminescence, photocurrent response, EIS and SPV measurements. Furthermore, in situ FTIR and LSV measurements revealed that doping cobalt ions can facilitate both CO₂ reduction and H₂O oxidation. Consequently, the prepared Co@Cs₃Sb₂Br₉/Sb₄O₅Br₂ heterostructure achieves excellent performance for photocatalytic CO₂ reduction, achieving a record-high electron consumption rate of 840 μmol g⁻¹ h⁻¹, which significantly surpasses that of other halide perovskite-based materials under similar conditions. The proposed direct partial transformation strategy opens up a new avenue to enhance spatial photogenerated carrier separation in halide perovskite-based heterostructures, and this approach could potentially be extended to the development of other heterostructure photocatalysts.

4. Experimental Section

Preparation of Sb₄O₅Br₂ Nanosheets: Sb₄O₅Br₂ nanosheets were synthesized by the solvothermal synthesis method. First, 0.25 mmol of SbBr₃ (90.37 mg) and 9 mL of ethanol were added into a beaker and completely dissolved using ultrasound. The mixture was then stirred for 30 min. Next, 0.25 mmol of KBr was dispersed in 1 mL of deionized water and added dropwise to the above solution. After stirring for an additional 30 min, the mixture was transferred to a Teflon-line autoclave (25 mL) and maintained at 120 °C for 24 h. After cooling to room temperature, the mixture was washed with deionized water and ethanol and then dried at 60 °C overnight.

Preparation of Cs₃Sb₂Br₉/Sb₄O₅Br₂ Heterostructures: First, 5 mg of Sb₄O₅Br₂ and 2 mL of isopropyl alcohol solution were added into a 5 mL flask. The compound was ultrasonicated for 30 min to ensure thorough dispersion. A methanol solution of CsBr (20 mg mL⁻¹) was then added to the mixture under vigorous stirring and kept stirring for an additional 10 min. An isopropyl alcohol solution of HBr (V:V = 10:1) was injected into the mixture and kept stirring for another 5 min. Finally, the mixture was centrifuged at 5000 rpm for 3 min.

Preparation of Cs₃Sb₂Br₉ Nanocrystals: Cs₃Sb₂Br₉ nanocrystals were synthesized by the antisolvent precipitation method. First, the precursor solution of Cs₃Sb₂Br₉ was prepared by mixing 76 mg of CsBr, 86 mg of SbBr₃, and 3 mL of dimethyl sulfoxide solution in a 10 mL glass vial. After complete dissolution, a 0.4 M Cs₃Sb₂Br₉ precursor solution was obtained. Then, 300 μL Cs₃Sb₂Br₉ precursor solution was added dropwise to 3 mL of isopropyl alcohol under vigorous stirring, resulting in a rapid color change to yellowish green. After stirring for 5 min, the mixture was centrifuged at 7000 rpm for 3 min. The obtained suspension was washed with isopropyl alcohol, and the precipitation was dried in a vacuum oven at 60 °C for subsequent use.

Preparation of Cs₃Sb₂Br₉:Sb₄O₅Br₂ Heterostructures: First, 5 mg of Sb₄O₅Br₂ and 5 mg of Cs₃Sb₂Br₉ were dispersed in 2 mL of isopropyl alcohol, and then ultrasonicated for 30 min to ensure thorough dispersion. The mixture was stirred for 2 h afterward. After stirring, the mixture was centrifuged at 7000 rpm for 3 min, and the precipitates were dried in a vacuum oven at 60 °C.

Preparation of $\text{Co}@\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ Heterostructures: The synthesis process of $\text{Co}@\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$ was similar to that of $\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{Sb}_4\text{O}_5\text{Br}_2$, except that an adding methanol solution CsBr and CoBr_2 (0.05 M) was added to replace pure CsBr methanol solution in the initial step.

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

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

carrier separation, CO_2 reduction, heterostructure, lead-free halide perovskite, photocatalysis

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