

A Versatile Self-Templating Approach for Constructing Ternary Halide Perovskite Heterojunctions to Achieve Concurrent Enhancement in Photocatalytic CO₂ Reduction Activity and Stability

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Metal halide perovskite (MHP)-based photocatalysts encounter significant stability challenges in water-containing systems, posing a major obstacle to their application in artificial photosynthesis. Herein, an innovative and universal strategy is present to create MHP-based ternary heterojunctions based on a self-templating method. A series of composite catalysts featuring sandwich hollow structures are constructed, with MHPs such as CsPbBr₃, Cs₃Bi₂I₉, Cs₃Sb₂Br₉, and Cs₂AgBiBr₆ serving as the intermediate layers. The unique sandwich structure effectively shields MHPs from direct water contact, allowing MHP-based photocatalysts to exhibit exceptional stability in water-containing photocatalytic environments for durations exceeding 200 h. Furthermore, the hollow design ensures complete contact between the reaction substrates with both the oxidation and reduction functional areas. Compared to single perovskite materials, MHP-based ternary heterojunction photocatalysts exhibit stronger oxidation capability and improved charge separation efficiency, leading to a substantial enhancement in photocatalytic CO₂ reduction performance. Notably, the ternary heterojunction with CsPbBr₃ as the intermediate layer achieves an electron consumption rate of up to 1824 μmol g⁻¹ h⁻¹ for CO₂ reduction, which is far superior to other reported MHP-based catalysts under similar conditions. This study provides a potent strategy for simultaneously enhancing the stability and activity of MHP-based photocatalysts, paving the way for their potential applications in artificial photosynthesis.

for mitigating the energy crisis and fostering sustainable development.^[1,2] In this process, the inherent chemical inertia of CO₂ and the sluggish kinetics of H₂O oxidation necessitate photocatalysts with robust light-harvesting capabilities and long carrier lifetimes.^[3,4] However, most of the developed photocatalysts exhibit limited light-harvesting abilities,^[5] and their carrier lifetimes, which are measured in nanoseconds or even picoseconds,^[6] are insufficient for enabling long-range transport and efficient utilization of photogenerated carriers.^[7] Recently, metal halide perovskites (MHPs), characterized by exceptional photophysical properties,^[8] have emerged as potential research hotspots in the development of high-performance artificial photosynthesis catalysts.^[9,10] Nevertheless, the ionic nature of MHPs introduces inherent instability under high polarity conditions,^[11,12] posing considerable challenges for the construction of artificial photosynthesis systems in aqueous-rich environments.^[13,14] Additionally, MHPs suffer from a lack of sufficient catalytic active sites^[15] and limited CO₂ adsorption capabilities,^[16] which further hinder their efficiency in photocatalytic

reactions. Therefore, overcoming these obstacles to fully harness the potential of MHPs is crucial for advancing their application in the field of artificial photosynthesis.

To tackle the aforementioned challenges, MHPs are often safeguarded by constructing core-shell structures^[17–19] and adopting spatial confinement strategies.^[20–22] Although these methods successfully boost the stability and carrier separation efficiency of MHP-based catalysts, they suffer from limited reaction activity due to the restricted accessibility between the inner layer and the reactant substrates. To date, there are still very few examples of efficient and stable MHP-based photocatalysts. Inspired by the layered structure of MHP-based solar cells,^[23–26] we have attempted to devise a sandwich-structured MHP ternary heterojunction recently, with lead-free Cs₃Bi₂I₉ serving as the core

1. Introduction

Mimicking natural photosynthesis to convert CO₂ and H₂O into high-value chemicals and O₂ represents a pivotal pathway

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The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adfm.202423656>

DOI: 10.1002/adfm.202423656

light-harvesting layer, flanked by semiconductors dedicated to H_2O oxidation and CO_2 reduction, respectively. As anticipated, the resultant $\text{TiO}_2/\text{Cs}_3\text{Bi}_2\text{I}_9/\text{g-C}_3\text{N}_4$ ternary heterojunction^[27] achieved synchronous improvements in photocatalytic activity and stability. However, the sacrificial templating method employed in this preparation process requires strongly corrosive or alkaline reagents for template removal,^[28,29] which can easily lead to the dissociation of amphoteric metal oxides (such as Sb_2O_3 and PbO) that act as intermediates of MHP synthesis (Figure S1, Supporting Information). Therefore, exploring a more universal and mild strategy for constructing MHP-based ternary heterojunctions is crucial for advancing the extensive application of MHPs in the field of artificial photosynthesis.

Herein, inspired by the spontaneous formation of unique hollow structures derived from metal–organic frameworks (MOFs) after calcination (Figure S2, Supporting Information),^[30–32] we introduce an universal strategy for constructing ternary heterostructures based on the self-templating method. Initially, the MOF (MIL-125-NH_2) serves as a template for the in situ growth of a layer of MHP intermediate on its surface. Following calcination, MIL-125-NH_2 is converted into hollow TiO_2 , serving as the oxidation unit. Subsequently, graphdiyne (GDY) is grown in situ on the surface of the MHP intermediate, functioning as the reduction unit. Ultimately, the intermediate layer is converted into MHP, achieving the construction of the ternary heterojunction. This approach avoids the extreme chemical environments required by the sacrificial templating method, and effectively protects the MHP intermediate. Furthermore, the ternary heterojunction system facilitates the creation of dual built-in electric fields, enabling rapid separation and transport of carriers. Experimental findings reveal that all the MHP-based photocatalysts ($\text{TiO}_2/\text{MHP}/\text{GDY}$, with MHP = CsPbBr_3 , $\text{Cs}_3\text{Bi}_2\text{I}_9$, $\text{Cs}_3\text{Sb}_2\text{Br}_9$, or $\text{Cs}_2\text{AgBiBr}_6$) prepared via the self-templating method exhibit exceptional photocatalytic activity and stability, showcasing the immense potential of this strategy in enhancing the activity and stability of MHP-based photocatalysts. Notably, the ternary heterojunction based on CsPbBr_3 achieves an unprecedented electron consumption rate of $1825 \mu\text{mol g}^{-1} \text{h}^{-1}$ for photocatalytic CO_2 reduction, while maintaining stability exceeding 200 h in water-containing systems.

2. Results and Discussion

2.1. Preparation and Characterization of $\text{TiO}_2/\text{MHP}/\text{GDY}$ Ternary Heterojunction

All ternary heterojunctions were prepared by the self-templating method combined with sequential deposition technology, as outlined in the Experimental Section. Considering $\text{TiO}_2/\text{CsPbBr}_3/\text{GDY}$ as an representative example (Figure 1a), the process began with the synthesis of the MIL-125-NH_2 template via a solvothermal method.^[33] Zeta potential measurement confirmed that its surface carries a negative charge of -26.45 mV (Figure S3, Supporting Information). Subsequently, the template, endowed with a negative surface charge, selectively adsorbed Pb^{2+} resulting from the hydrolysis of lead acetate trihydrate, followed by the in situ deposition of stable metal complex with the assistance of urotropine. Upon high-temperature calcination, the template transformed into $\text{TiO}_2/\text{PbTiO}_3$ with a hollow

structure and a positively charged surface of 31.01 mV (Figure S3, Supporting Information), enabling the directional adsorption of negatively charged hexakis-[(trimethylsilyl)ethynyl]benzene (HEB-TMS) monomer (-22.34 mV ; Figure S3, Supporting Information) and the subsequent in situ growth of GDY^[34] on its surface. Upon the formation of $\text{TiO}_2/\text{PbTiO}_3/\text{GDY}$, Cs-oleate is introduced as the halide perovskite precursor, enabling the selective in situ transformation of PbTiO_3 into CsPbBr_3 with the assistance of HBr . In this process, TiO_2 and GDY maintain their stability in the presence of HBr (Figures S4, S5, Supporting Information), whereas PbTiO_3 is decomposed by HBr to liberate Pb^{2+} (Figure S6a, Supporting Information). Given the low formation energy of CsPbBr_3 , the liberated Pb^{2+} readily combines with Cs-oleate and Br^- to form CsPbBr_3 in situ, effectively achieving the selective conversion of PbTiO_3 to CsPbBr_3 (Figure S6b,c, Supporting Information). This strategy overcomes the deficiencies in the sacrificial template method, ensuring efficient and controllable reactions through precise charge-directed synthesis, thereby providing a reliable approach for the preparation of high-quality ternary heterojunctions.

The morphological evolution of intermediates during the preparation of ternary heterojunctions was analyzed using high-resolution scanning electron microscopy (HRSEM) and high-resolution transmission electron microscopy (HRTEM). As depicted in Figure 1b, the MIL-125-NH_2 template exhibits a nanodisk morphology with a length of approximately 400 nm and a smooth surface. After calcination in an air atmosphere, the original morphology and surface state of MIL-125-NH_2 are largely preserved (Figure S7, Supporting Information). Following the in situ growth of a PbTiO_3 layer, the material surface undergoes significantly roughening (Figure 1c). Subsequent reactions result in the uniform coating of GDY on the outer layer, ultimately forming the $\text{TiO}_2/\text{PbTiO}_3/\text{GDY}$ composite (Figure 1d). HRTEM image indicates that the in situ conversion of PbTiO_3 to CsPbBr_3 barely alters the sample morphology (Figure 1e), confirming the structural stability of the composite. Energy-dispersive X-ray spectroscopy (EDS) mapping measurements were employed to delve deeper into the elemental distribution within the $\text{TiO}_2/\text{CsPbBr}_3/\text{GDY}$ composite. As illustrated in Figure 1f–k, Ti, O, Cs, Pb, Br, and C are uniformly dispersed throughout the sample, providing preliminary confirmation for the successful preparation of ternary heterojunction with a hollow structure. After introducing Co active sites during GDY synthesis, the thickness of the outer GDY layer remained nearly constant (approximately 19 nm, Figures S8, S9, Supporting Information), and there was no discernible impact on the sample morphology (Figure S10, Supporting Information). These findings suggest that the introduction of Co does not hinder the preparation of GDY. Notably, replacing the metal source with $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and acid source with HI enables the preparation of ternary heterojunctions $\text{TiO}_2/\text{Cs}_3\text{Bi}_2\text{I}_9/\text{GDY}$ (Figure S11, Supporting Information), while replacing the metal source with antimony triacetate can prepare $\text{TiO}_2/\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{GDY}$ (Figure S12, Supporting Information). When $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ serves as the metal source, the introduction of additional AgBr during the conversion process allows for the obtainment of $\text{TiO}_2/\text{Cs}_2\text{AgBiBr}_6/\text{GDY}$ (Figure S13, Supporting Information). These results underscore the extensive versatility of the self-templating approach in constructing a diverse range of MHP systems.

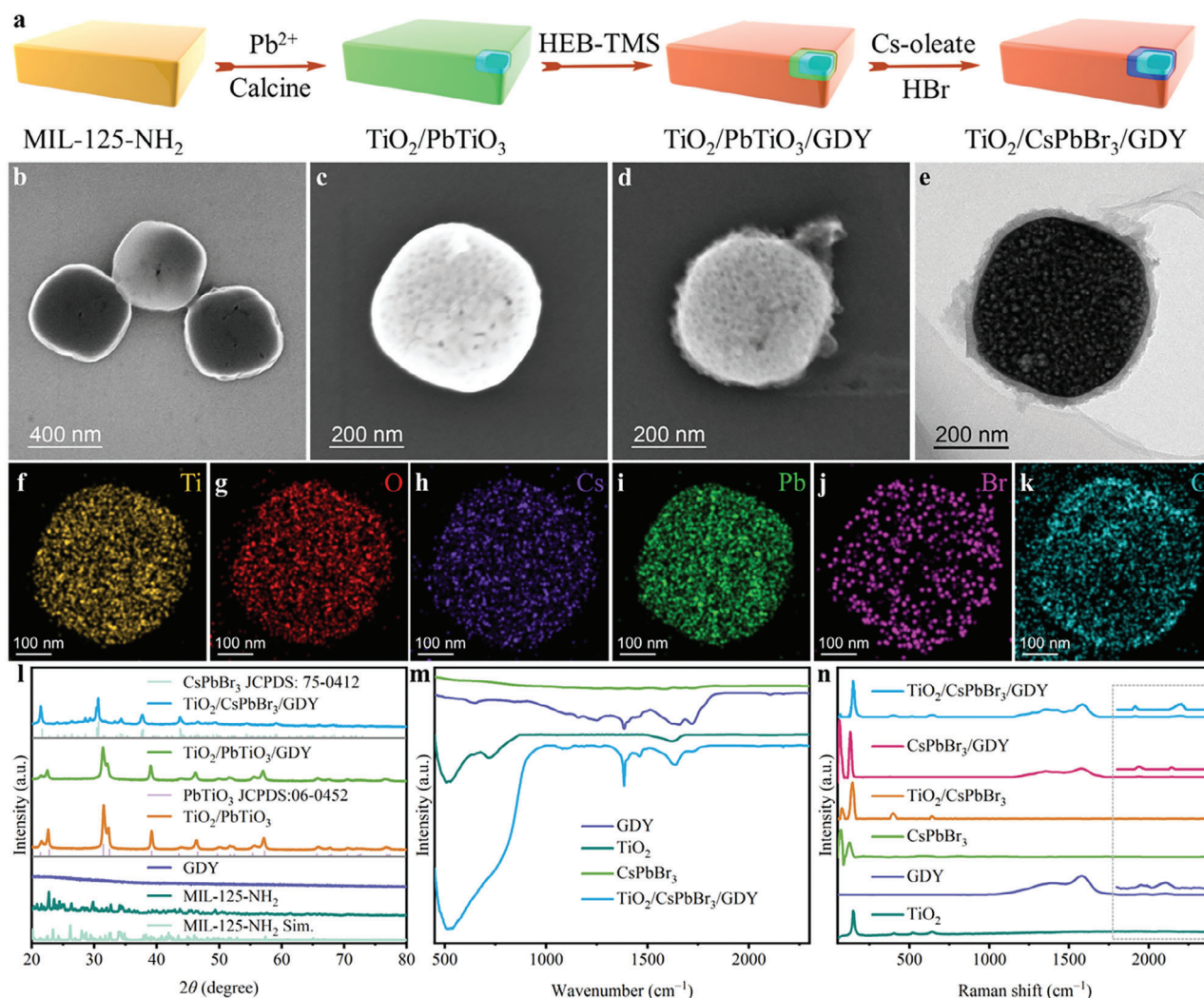


Figure 1. a) Schematic illustration of the synthesis process of $\text{TiO}_2/\text{CsPbBr}_3/\text{GDY}$. HRSEM images of b) MIL-125- NH_2 , c) $\text{TiO}_2/\text{PbTiO}_3$, d) $\text{TiO}_2/\text{PbTiO}_3/\text{GDY}$, e) HRTEM image of $\text{TiO}_2/\text{CsPbBr}_3/\text{GDY}$. f–k) EDS elemental mapping images of $\text{TiO}_2/\text{PbTiO}_3/\text{GDY}$ composite: f) Ti, g) O, h) Cs, i) Pb, j) Br, k) C. l) XRD patterns of MIL-125- NH_2 , GDY, $\text{TiO}_2/\text{PbTiO}_3$, $\text{TiO}_2/\text{PbTiO}_3/\text{GDY}$, and $\text{TiO}_2/\text{CsPbBr}_3/\text{GDY}$. m) FTIR spectra of GDY, TiO_2 , CsPbBr_3 , and $\text{TiO}_2/\text{CsPbBr}_3/\text{GDY}$. n) Raman spectra of TiO_2 , GDY, CsPbBr_3 , $\text{TiO}_2/\text{CsPbBr}_3$, $\text{CsPbBr}_3/\text{GDY}$, and $\text{TiO}_2/\text{CsPbBr}_3/\text{GDY}$.

Powder X-ray diffraction (PXRD) measurements were further carried out to investigate the structural characteristics of ternary heterojunctions. As shown in Figure 1l, the XRD pattern of MIL-125- NH_2 aligns perfectly with the simulated pattern (Figure S14, Supporting Information),^[35] indicating the successful synthesis of the template. After calcination in an air atmosphere, the resultant XRD pattern corresponds well with the anatase TiO_2 (Figure S15, Supporting Information, JCPDS: 21–1272),^[36] suggesting that the MIL-125- NH_2 template can be transformed to TiO_2 through high-temperature calcination. Moreover, when a metal complex is coated onto MIL-125- NH_2 and subsequently subjected to high-temperature calcination, the resulting XRD peaks match well with PbTiO_3 (JCPDS: 06–0452),^[37] which are sufficiently intense and can obscure the peaks associated with TiO_2 . Following the in situ growth of a GDY layer on the PbTiO_3 surface, there are no significant alterations in the XRD peaks, attributed to the weak crystallinity of GDY. Upon the transformation of PbTiO_3 , distinctive peaks corresponding to CsPbBr_3

(JCPDS: 75–0412) emerge,^[38] further affirming the successful fabrication of the $\text{TiO}_2/\text{CsPbBr}_3/\text{GDY}$ composite. The XRD results for the remaining three ternary heterojunctions (Figures S16–S18, Supporting Information) also demonstrate similar regularity, validating that the combination of the self-templating method and the sequential deposition technique enables efficient and controllable synthesis of ternary heterojunctions.

The composition of the $\text{TiO}_2/\text{CsPbBr}_3/\text{GDY}$ ternary heterojunction was further examined with the Fourier transform infrared (FTIR) spectroscopy and Raman spectroscopy measurements. As presented in Figure 1m, the pristine CsPbBr_3 lacks IR peaks due to its ionic crystal property, whereas TiO_2 exhibits characteristic vibrational peaks belonging to Ti–O–Ti at 505 and 721 cm^{-1} .^[39] GDY displays multiple IR characteristic peaks, including those at 1384 and 1643 cm^{-1} arising from aromatic ring skeletal vibrations, and those at 2101 and 2174 cm^{-1} stemming from acetylene bond stretching vibrations.^[40] It is worth noting that all the aforementioned characteristic peaks are

detectable in $\text{TiO}_2/\text{CsPbBr}_3/\text{GDY}$ sample, confirming the inclusion of TiO_2 and GDY within the composite. Similarly, corresponding components are identifiable in the IR spectra of $\text{TiO}_2/\text{CsPbBr}_3$ and $\text{CsPbBr}_3/\text{GDY}$ binary heterojunctions, as well as other ternary heterojunctions (Figures S19–S22 and Table S1, Supporting Information). Raman spectra measurement results, exhibited in Figure 1n, can provide more insight into the material composition. Raman signals attributed to symmetric stretching vibrations of O–Ti–O (151 and 643 cm^{-1}) and bending vibrations of O–Ti–O^[41] (404 and 524 cm^{-1}) can be detected in TiO_2 . The characteristic peaks at 70 and 123 cm^{-1} of pristine CsPbBr_3 are assigned to $[\text{PbBr}_6]^{4-}$ octahedron vibration and Cs^+ ion motion,^[42] respectively. Pure GDY displays typical Raman peaks of carbon material, with the G-band at 1575 cm^{-1} arising from C–C bond vibrations and the D-band at 1378 cm^{-1} induced by intrinsic defects. Notably, Raman peaks at 1957 and 2106 cm^{-1} correspond to acetylene bonds ($\text{C}\equiv\text{C}$) and conjugated chains ($-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-$),^[43] respectively, indicating the successful synthesis of GDY. In the Raman spectrum of $\text{TiO}_2/\text{CsPbBr}_3/\text{GDY}$, the characteristic peaks of CsPbBr_3 , TiO_2 , and GDY are observed at approximately 75 , 150 , 399 , 517 , 647 , 1914 , and 2194 cm^{-1} , respectively, further confirming the composition of the $\text{TiO}_2/\text{CsPbBr}_3/\text{GDY}$ ternary heterojunction. Similar conclusions can be drawn from binary heterojunctions ($\text{TiO}_2/\text{CsPbBr}_3$, $\text{CsPbBr}_3/\text{GDY}$) and other ternary heterojunctions (Figures S23–S25 and Table S2, Supporting Information). Furthermore, inductively coupled plasma-mass spectrometry (ICP-MS) analysis (Figure S26 and Table S3, Supporting Information) revealed that the mass percentages of TiO_2 , MHP (MHP = CsPbBr_3 , $\text{Cs}_3\text{Bi}_2\text{I}_9$, $\text{Cs}_3\text{Sb}_2\text{Br}_9$, or $\text{Cs}_2\text{AgBiBr}_6$), and GDY in the $\text{TiO}_2/\text{MHP}/\text{GDY}$ ternary heterojunctions range from 29 to 48% , 40 to 64% , and 7 to 18% , respectively. These findings strongly suggest the successful preparation of the ternary heterojunctions.

2.2. Energy Band Structures and Interfacial Interaction of $\text{TiO}_2/\text{MHP}/\text{GDY}$ Ternary Heterojunction

The thermodynamic properties of components in $\text{TiO}_2/\text{MHP}/\text{GDY}$ ternary heterojunctions were determined using the ultraviolet–visible diffuse reflectance spectroscopy (UV–Vis DRS), ultraviolet photoelectron spectroscopy (UPS), and Mott–Schottky curve measurements. As illustrated in UV–vis DRS spectra (Figure S27, Supporting Information), TiO_2 exhibits an absorption edge at approximately 402 nm , demonstrating a relatively weak photon response in the visible light region, whereas CsPbBr_3 displays a strong and broad response up to 548 nm . Consequently, heterojunctions incorporating CsPbBr_3 , namely $\text{TiO}_2/\text{CsPbBr}_3/\text{GDY}$, $\text{TiO}_2/\text{CsPbBr}_3$, and $\text{CsPbBr}_3/\text{GDY}$, all exhibit robust visible light responses. While GDY possesses full-spectrum absorption, its low coefficient implies that the primary contribution to light-harvesting capability of CsPbBr_3 -based composites comes from CsPbBr_3 . Subsequently, the UV–vis DRS data were converted into Tauc plots (Figure S28a–c, Supporting Information) to ascertain the optical band gaps (E_g) of TiO_2 , CsPbBr_3 , and GDY, which were found to be 3.14 , 2.33 , and 1.64 eV , respectively. UPS results (Figure 2a) were analyzed to calculate the valence band maximum (VBM)

potentials of TiO_2 , CsPbBr_3 , and GDY to be 2.95 , 1.69 , and 1.22 V versus the standard hydrogen electrode (vs. SHE), respectively. Additionally, XPS valence band spectra further confirmed the VBM offset of 1.27 eV between TiO_2 and CsPbBr_3 , and of 0.44 eV between CsPbBr_3 and GDY (Figure 2b), indicating a staggered band alignment between TiO_2 and CsPbBr_3 , and a straddling gap band alignment between CsPbBr_3 and GDY (Figure 2c). Mott–Schottky curve measurements (Figure S29a–c, Supporting Information) revealed that the flat-band potentials of TiO_2 , GDY, and CsPbBr_3 are -0.21 , -0.41 , and -0.66 V (vs. SHE), respectively, which are consistent with the results of UPS and XPS measurements. Comparable thermodynamic information can be obtained from other MHP-based ternary heterojunctions (Figures S28–S33, Supporting Information).

Furthermore, the Fermi levels of TiO_2 , CsPbBr_3 , and GDY were determined based on UPS measurements at -5.10 , -4.26 , and -3.94 eV (relative to the vacuum level), with the band structure diagram portrayed in Figure 2d,i. When the components of the ternary heterojunction are brought into intimate contact, the aforementioned disparities in Fermi levels will initiate spontaneous migration of free electrons, ultimately achieving an equilibrium state among the Fermi energy levels. Specifically, at the interface of $\text{TiO}_2/\text{CsPbBr}_3$, CsPbBr_3 functions as a donor of free electrons due to its higher Fermi energy level, inducing the transfer of free electrons from CsPbBr_3 to TiO_2 . This process establishes a built-in electric field (BEF, Figure 2d,ii) directed from CsPbBr_3 to TiO_2 . It is worth noting that the formation of the BEF is accompanied by the bending of energy bands at the contact interface, specifically manifested as the TiO_2 energy band bending downward and the CsPbBr_3 energy band bending upward. Analogously, at the $\text{CsPbBr}_3/\text{GDY}$ interface, CsPbBr_3 transforms into the acceptor of free electrons owing to its lower Fermi level, leading to the flow of interfacial electrons from GDY to CsPbBr_3 and forming a BEF directed from GDY to CsPbBr_3 , simultaneously causing the energy band of CsPbBr_3 to bend downward and the energy band of GDY to bend upward. Notably, the BEF can further facilitate the directional migration of photogenerated carriers at the heterojunction interface. As depicted in Figure 2d,iii, under the influence of BEF and band bending, photogenerated electrons in the conduction band (CB) of TiO_2 are inclined to migrate toward the valence band (VB) of CsPbBr_3 , thereby promoting efficient separation of photogenerated carriers in $\text{TiO}_2/\text{CsPbBr}_3$ heterojunction through a Z-scheme charge transfer mechanism. Moreover, the CB and VB of CsPbBr_3 are higher and deeper, respectively, compared to those of GDY, where the direction of the BEF promotes the transfer of photogenerated electrons from the CB of CsPbBr_3 to the CB of GDY. However, the band bending poses a hindrance to the migration of photogenerated holes from CsPbBr_3 to GDY. Consequently, the photogenerated carriers at the $\text{CsPbBr}_3/\text{GDY}$ interface adhere to a typical type-I heterojunction transfer pathway for separation.

2.3. Separation and Transmission of Photogenerated Carriers within $\text{TiO}_2/\text{MHP}/\text{GDY}$ Ternary Heterojunction

The direction of free electron migration at the heterojunction interface can be confirmed through high-resolution X-ray

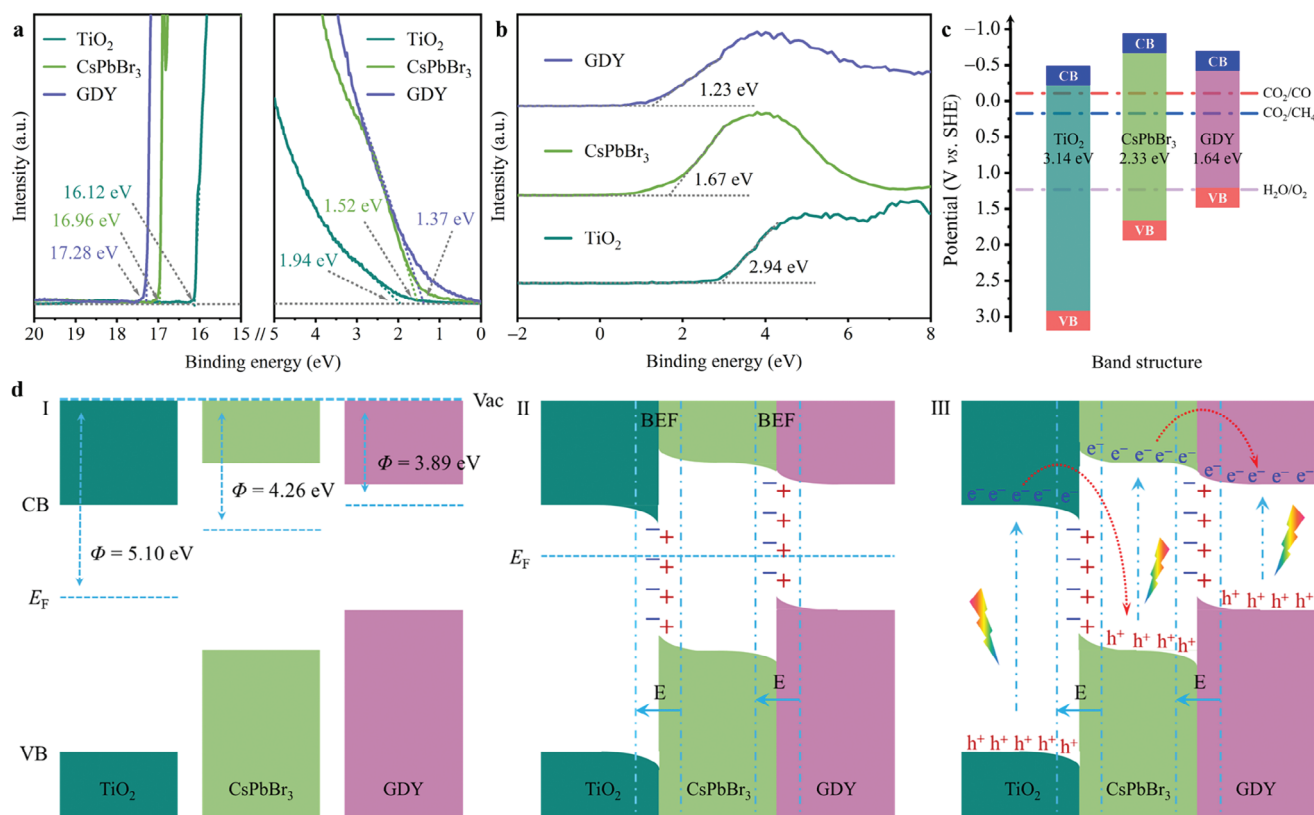


Figure 2. a) UPS spectra, b) XPS valence spectra and c) energy band structure diagrams of TiO₂, CsPbBr₃ and GDY. d) Energy band structure and charge transfer in TiO₂/CsPbBr₃/GDY: Energy band structures of TiO₂, CsPbBr₃, and GDY before I) and after II) contact; III) Charge transfer pathway in TiO₂/CsPbBr₃/GDY under illumination. Φ denotes the work function, and its value is the negative counterpart of the corresponding Fermi energy level (E_F), E denotes the electric field, and the direction of the arrow indicates the direction of the electric field.

photoelectron spectroscopy (XPS) measurements. As displayed in Figure 3a, the characteristic peaks of Cs 3d, Pb 4f, and Br 3d in TiO₂/CsPbBr₃ shift toward higher binding energies (0.15–0.24 eV) relative to those in CsPbBr₃, whereas the binding energies of Ti 3d and O 1s in TiO₂/CsPbBr₃ exhibit a significant shift toward lower values (0.20–0.24 eV) compared to those in TiO₂ (Figure S34, Supporting Information). These changes indicate that free electrons migrate from CsPbBr₃ to TiO₂. For the CsPbBr₃/GDY heterojunction (Figure 3b), the binding energies of Cs 3d, Pb 4f, and Br 3d undergo a negative shift (0.11–0.30 eV) compared to CsPbBr₃, while C 1s experiences a positive shift (0.26 eV) relative to GDY (Figure S35, Supporting Information), demonstrating the free electron transfer occurs from GDY to CsPbBr₃. These significant variations among element binding energies further suggest the presence of a robust electron coupling effect at the interface upon the formation of heterojunctions, which is pivotal for facilitating the efficient separation of photogenerated carriers.

In-situ XPS measurements were conducted to further validate the migration direction of photogenerated carriers (Figures S36, S37, Supporting Information). As depicted in Figure 3c, the binding energies of Cs 3d, Pb 4f, and Br 3d in TiO₂/CsPbBr₃ decrease by 0.10–0.25 eV under illumination, while those of Ti 3d and O 1s increase by 0.20–0.24 eV. These shifts suggest that photogenerated electrons and holes accumu-

late in CsPbBr₃ and TiO₂, respectively, thereby confirming that the separation of photogenerated carriers at the TiO₂/CsPbBr₃ heterojunction interface follows a Z-scheme charge transfer mode. For the CsPbBr₃/GDY heterojunction (Figure 3d), the binding energies of Cs 3d, Pb 4f, and Br 3d shift positively (0.12–0.49 eV) upon illumination, while the peaks of C 1s shift to lower binding energy (0.24–0.33 eV). These results indicate the enrichment of photogenerated electrons in GDY, further verifying that the separation of photogenerated carriers follows a type-I transfer pathway.

To further elucidate the transfer mechanism of photogenerated carriers, hydroxyl radical ($\cdot\text{OH}$) and furfuryl alcohol-oxidized carbon radical ($\text{R}\cdot$) trapping experiments were carried out using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as the capturing agent. As illustrated in Figure 3e, the absence of $\cdot\text{OH}$ characteristic signal peaks under dark conditions confirms that light illumination is essential for $\cdot\text{OH}$ generation. Additionally, no DMPO- $\cdot\text{OH}$ signal can be observed with CsPbBr₃ as the photocatalyst, attributed to its insufficient thermodynamic driving force for oxidizing H₂O into OH (2.40 V vs. SHE).^[44] However, the signal intensity of DMPO- $\cdot\text{OH}$ in TiO₂/CsPbBr₃ is significantly stronger than that in TiO₂, suggesting an effective retention of photogenerated holes in the VB of TiO₂ in TiO₂/CsPbBr₃, which is indicative of the Z-scheme transfer mechanism of photogenerated carriers at the TiO₂/CsPbBr₃

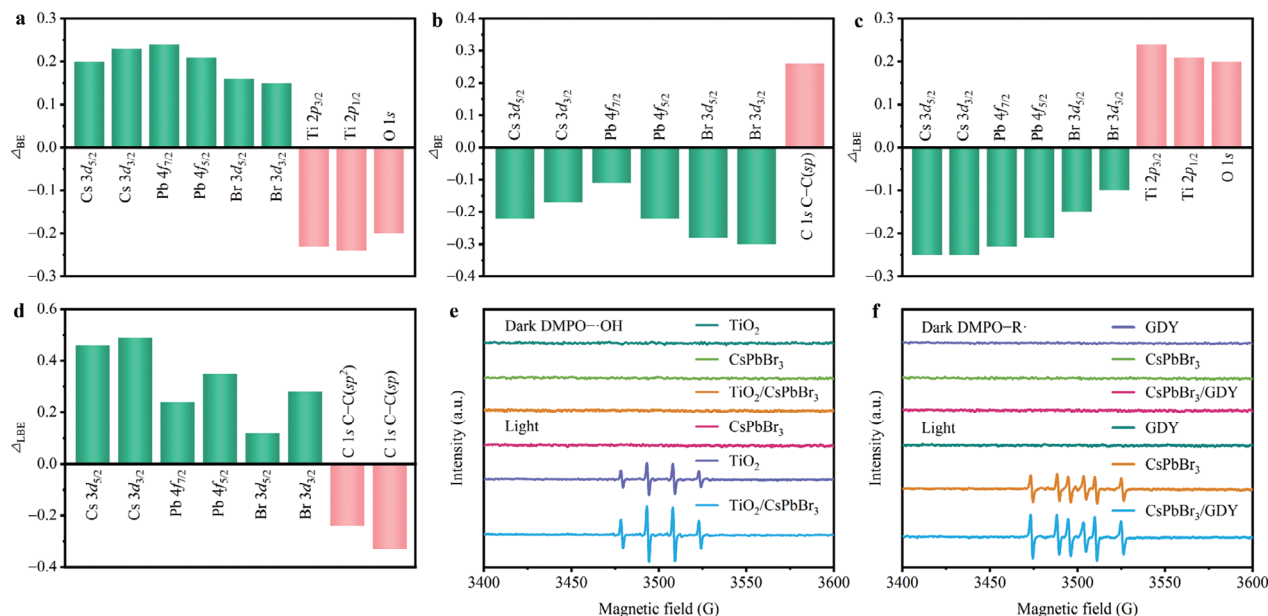


Figure 3. Binding energy shifts (Δ_{BE}) of elements in a) TiO₂/CsPbBr₃ relative to TiO₂ and CsPbBr₃, and b) CsPbBr₃/GDY compared to CsPbBr₃ and GDY under dark derived from high-resolution XPS measurements. Light-induced binding energy shifts (Δ_{LBE}) of elements in c) TiO₂/CsPbBr₃ and d) CsPbBr₃/GDY derived from ISI-XPS measurements. e) EPR spectra of DMPO–OH in TiO₂, CsPbBr₃, and TiO₂/CsPbBr₃. f) EPR spectra of DMPO–R· in CsPbBr₃, GDY, and CsPbBr₃/GDY.

interface. Given the weak oxidation abilities of photogenerated holes in CsPbBr₃ and GDY, R· radicals produced by the oxidation of furan alcohols were selected as the capture targets to explore the photogenerated carrier transfer mechanism at the CsPbBr₃/GDY interface. As shown in Figure 3f, none of the samples exhibit the DMPO–R· signals under dark conditions. Upon irradiation, the DMPO–R· signals also cannot be observed in GDY, because the photogenerated holes in GDY are unable to drive furfuryl alcohol oxidation (1.44 V vs. SHE).^[45] In contrast, CsPbBr₃ demonstrates the capability to oxidize furfuryl alcohol with distinct DMPO–R· signals. Notably, there is a noticeable increase in the DMPO–R· signal upon the formation of the CsPbBr₃/GDY heterojunction, highlighting the retention and utilization of photogenerated holes in the VB of CsPbBr₃. This phenomenon suggests the presence of a type-I transfer mechanism at the CsPbBr₃/GDY interface. Therefore, the TiO₂/CsPbBr₃/GDY ternary heterojunction exhibits a coexistence of Z-scheme and type-I photogenerated carrier transfer mechanisms.

The dynamics of photogenerated carriers were thoroughly investigated using nanosecond transient absorption spectroscopy measurements. As presented in Figure 4 a–d, negative signals attributed to ground-state bleaching (GSB) of CsPbBr₃ emerge near 520 nm under excitation with a 440 nm laser, indicating the filling of the CB of CsPbBr₃ by excited electrons. Further monitoring of the kinetic recovery traces of the GSB peaks is performed to assess the deactivation processes of photogenerated excitons in different materials (Figure 4e). The multi-exponential fitting result reveals a lifetime of 19.81 ns for the delayed GSB recovery process in CsPbBr₃ (Table S4, Supporting Information). When CsPbBr₃ forms binary heterojunctions with TiO₂ or GDY, the accelerated-GSB recovery processes yield lifetimes of

9.25 ns and 14.23 ns, respectively. Notably, TiO₂/CsPbBr₃/GDY exhibits the fastest delayed GSB recovery process with a lifetime of 5.69 ns, suggesting that the dual built-in electric fields significantly enhance the charge transfer efficiency at the heterojunction interface. The photocurrent response (*I*–*t* curves) and electrochemical impedance spectroscopy (EIS) tests provide additional evidence supporting the enhancement of charge separation efficiency in the ternary heterojunction. As demonstrated in Figure 4f, the photocurrent intensities of TiO₂/CsPbBr₃ and CsPbBr₃/GDY are both higher than those of TiO₂, CsPbBr₃, and GDY individually, while TiO₂/CsPbBr₃/GDY exhibits the highest photocurrent intensity, which validates the promotion effect of the built-in electric fields on interfacial charge separation. Furthermore, the Nyquist plots reveal that the semicircle diameter of TiO₂/CsPbBr₃/GDY is significantly smaller compared to those of TiO₂, CsPbBr₃ and corresponding binary heterojunctions (Figure S38, Supporting Information). Combined with similar trends observed in other ternary heterojunctions under the same tests (Figures S39–S44, Supporting Information), it can be inferred that the dual built-in electric fields in the ternary heterojunction system significantly promote interfacial charge separation.

2.4. Photocatalytic CO₂ Reduction Activity and Stability of TiO₂/MHP/GDY

The activity of artificial photosynthesis was systematically evaluated using a gas–solid reaction setup apparatus with CO₂ and water as raw materials and a xenon lamp as light source (Figure S45, Supporting Information). Gas chromatographic analysis revealed that the primary reduction product of all

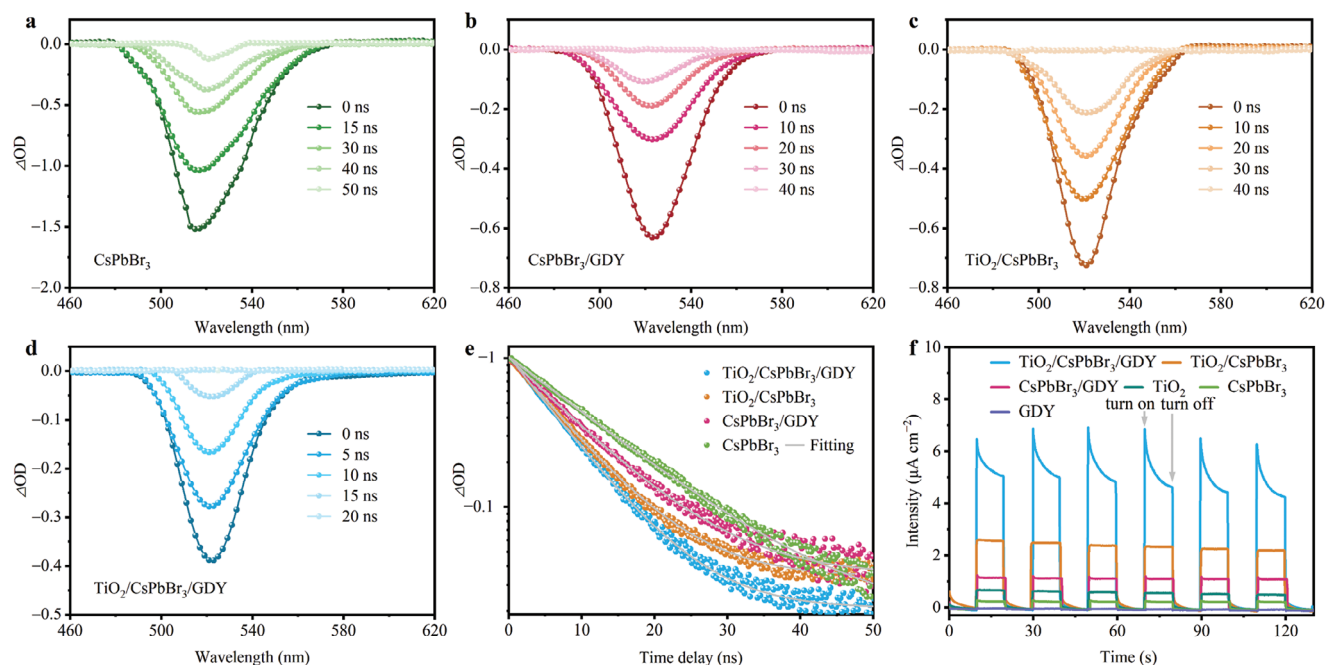


Figure 4. Nanosecond transient absorption (ns-TA) spectroscopies of a) CsPbBr₃, b) CsPbBr₃/GDY, c) TiO₂/CsPbBr₃, and d) TiO₂/CsPbBr₃/GDY at indicated delay times after 440 nm excitation. e) ns-TA kinetic plots of CsPbBr₃, CsPbBr₃/GDY, TiO₂/CsPbBr₃, and TiO₂/CsPbBr₃/GDY monitored at respective GSB peak. f) *I*-*t* curves of TiO₂, CsPbBr₃, GDY, CsPbBr₃/GDY, TiO₂/CsPbBr₃, and TiO₂/CsPbBr₃/GDY.

samples is CO, accompanied by trace amounts of CH₄ and negligible formic acid (GDY was excluded due to its inability to drive the water oxidation reaction for artificial photosynthesis, Table S5 and Figure S46, Supporting Information). As depicted in Figure 5a, TiO₂ with strong H₂O oxidizing ability achieves a moderate CO yield of 81 μmol g⁻¹ h⁻¹ for photocatalytic CO₂ reduction. Under the same conditions, CsPbBr₃, Cs₃Bi₂I₉, Cs₃Sb₂Br₉, and Cs₂AgBiBr₆, with moderate redox potentials and excellent light-absorption abilities, exhibit certain photocatalytic activities with CO yields of 53, 33, 42, and 66 μmol g⁻¹ h⁻¹, respectively. After combining MHP with GDY to form binary heterojunctions, the CO yields of CsPbBr₃/GDY, Cs₃Bi₂I₉/GDY, Cs₃Sb₂Br₉/GDY, and Cs₂AgBiBr₆/GDY increase to 178, 100, 115, and 101 μmol g⁻¹ h⁻¹, respectively, owing to the improved charge separation efficiency. By integrating MHP with water oxidation catalyst TiO₂, both the water oxidation capability and charge separation efficiency are simultaneously enhanced, leading to a further improvement in photocatalytic CO₂ reduction performance. The corresponding binary heterojunctions TiO₂/CsPbBr₃, TiO₂/Cs₃Bi₂I₉, TiO₂/Cs₃Sb₂Br₉, and TiO₂/Cs₂AgBiBr₆ achieve CO yields of 296, 184, 247, and 238 μmol g⁻¹ h⁻¹, respectively. Notably, all TiO₂/MHP/GDY ternary heterojunctions demonstrate optimal photocatalytic activities compared to individual MHP and corresponding binary heterojunctions, with CO yields reaching 467, 271, 383, and 303 μmol g⁻¹ h⁻¹ for TiO₂/CsPbBr₃/GDY, TiO₂/Cs₃Bi₂I₉/GDY, TiO₂/Cs₃Sb₂Br₉/GDY, and TiO₂/Cs₂AgBiBr₆/GDY, respectively. This exceptional performance can be attributed to the unique dual BEF at the ternary heterojunction interfaces, which can facilitate efficient separation and transport of photogenerated carriers. Furthermore, the introduction of Co as a cocatalyst in TiO₂/CsPbBr₃/GDY ternary heterojunction can further boost the

CO yield to 711 μmol g⁻¹ h⁻¹, accompanied by a photogenerated electron consumption rate of 1825 μmol g⁻¹ h⁻¹, representing a 13-fold increase in CO yield compared to that of single CsPbBr₃ and far exceeding the currently reported halide perovskite-based photocatalysts (Figure 5b).

All of the aforementioned samples were subjected to the long-term photocatalytic test to validate the stability of sandwich-structured ternary heterojunctions, with the exception of pure GDY due to its inherent thermodynamic constraints. As illustrated in Figure 5c-f, the photocatalytic activities of MHPs (CsPbBr₃, Cs₃Bi₂I₉, Cs₃Sb₂Br₉, and Cs₂AgBiBr₆) undergo a significant decline after 24 h and reach a plateau at 72 h, rendering them impractical for sustained photocatalytic CO₂ reduction. When MHPs are combined with TiO₂ or GDY, the obtained binary heterojunctions can exhibit enhanced photocatalytic activities due to the efficient separation of photogenerated carriers. Nevertheless, binary heterojunctions also exhibit limited stability reaching a plateau in their catalytic performance after 96 h. In contrast, the TiO₂/MHP/GDY ternary heterojunctions simultaneously demonstrate exceptional photocatalytic activity and stability, maintaining consistent performance over a 200-h photocatalytic process. The virtually unchanged XRD patterns and HRSEM images of post-photocatalytic reactions can further confirm the stability of ternary heterojunctions (Figures S47, S48, Supporting Information). Notably, the XRD characteristic diffraction peaks of MHPs in TiO₂/MHP and MHP/GDY binary heterojunctions largely disappear after reaction, accompanied by the emergence of peaks corresponding to TiO₂ and GDY (Figures S49-S52, Supporting Information). This may be attributed to the gradual dissociation of MHPs when directly exposed to a water vapor environment, thereby compromising their overall stability.

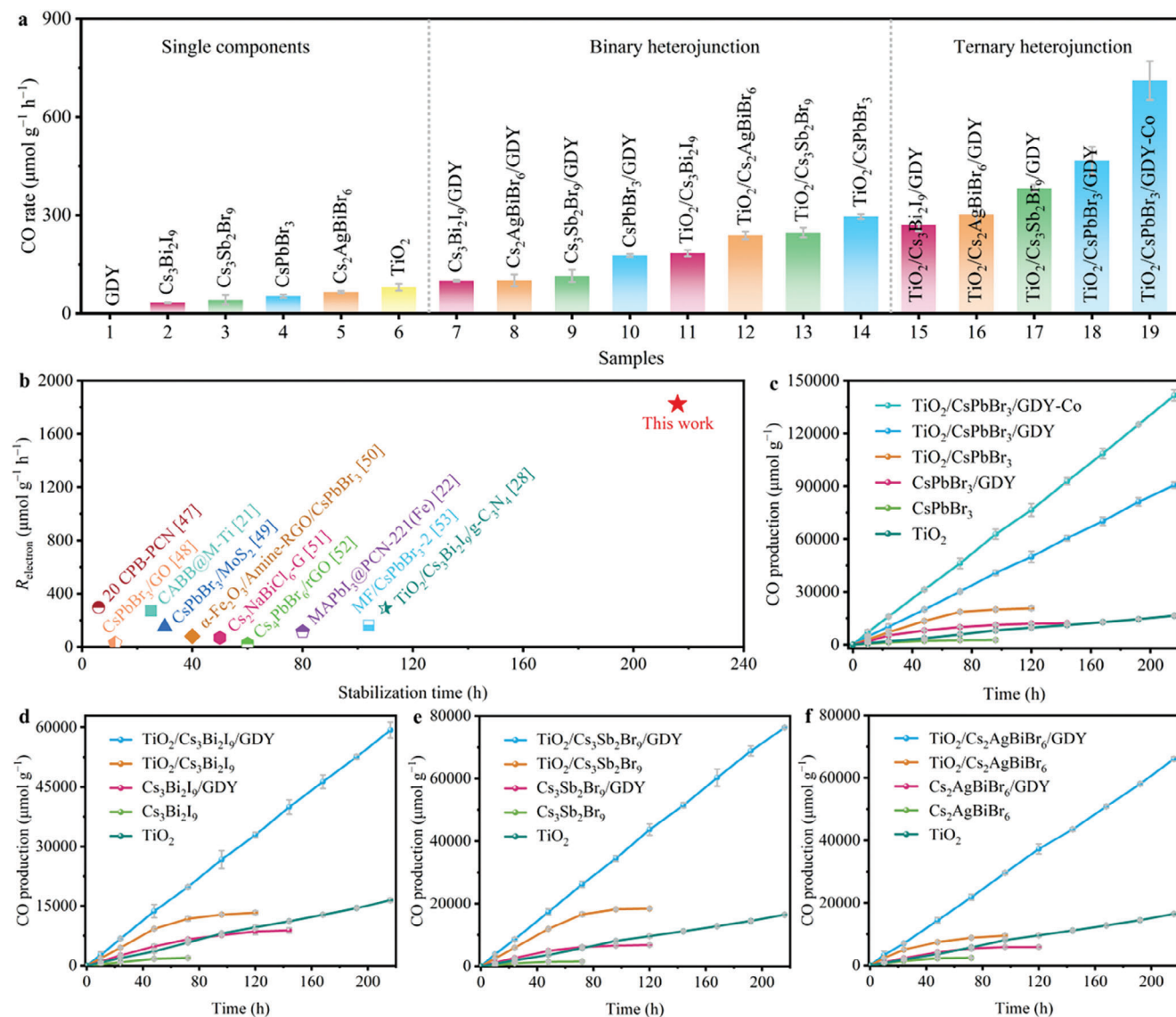


Figure 5. a) The CO generation rate under irradiation of 10 h. b) Comparative data of $\text{TiO}_2/\text{CsPbBr}_3/\text{GDY-Co}$ for CO_2 reduction with other reported MHP-based photocatalysts. c–f) CO production during the long-term photocatalytic CO_2 reduction with TiO_2 , MHPs, GDY, MHP/GDY, TiO_2/MHP , and $\text{TiO}_2/\text{MHP}/\text{GDY}$ (MHP = CsPbBr_3 , $\text{Cs}_3\text{Bi}_2\text{I}_9$, $\text{Cs}_3\text{Sb}_2\text{Br}_9$, or $\text{Cs}_2\text{AgBiBr}_6$) as the photocatalysts.

The stability origins of $\text{TiO}_2/\text{MHP}/\text{GDY}$ (MHP = CsPbBr_3 , $\text{Cs}_3\text{Bi}_2\text{I}_9$, $\text{Cs}_3\text{Sb}_2\text{Br}_9$, or $\text{Cs}_2\text{AgBiBr}_6$) ternary heterojunctions were explored relying on water contact angle measurements. As shown in Figures S53–S56 (Supporting Information), TiO_2 exhibits exceptional hydrophilicity with a water contact angle of 13.39° , which is beneficial to water oxidation half-reaction during the photocatalytic process. In contrast, CsPbBr_3 , $\text{Cs}_3\text{Bi}_2\text{I}_9$, $\text{Cs}_3\text{Sb}_2\text{Br}_9$, and $\text{Cs}_2\text{AgBiBr}_6$ demonstrate hydrophobicity with contact angles of 46.27° , 44.28° , 28.82° , and 41.54° , respectively. Notably, the pristine GDY shows the highest hydrophobicity with a contact angle of 66.62° , which is conducive to preventing the direct contact between internal MHPs and H_2O molecules. The contact angles of $\text{TiO}_2/\text{CsPbBr}_3$, $\text{TiO}_2/\text{Cs}_3\text{Bi}_2\text{I}_9$, $\text{TiO}_2/\text{Cs}_3\text{Sb}_2\text{Br}_9$, and $\text{TiO}_2/\text{Cs}_2\text{AgBiBr}_6$ are 45.17° , 41.23° , 27.89° , and 39.84° , respectively, suggesting that TiO_2 is tightly encapsulated by

MHPs. In addition, the contact angles for $\text{TiO}_2/\text{MHP}/\text{GDY}$ ternary heterojunctions are nearly identical to those of pure GDY, revealing that the intermediate MHP layers are tightly coated by the outermost GDY layer. It should be noted that although the ternary heterojunction is coated with hydrophobic GDY on its outer layer, the N_2 adsorption measurement of the material revealed the presence of 4.5 nm pore diameters within the ternary heterojunction (Figure S57, Supporting Information), ensuring that H_2O vapor can enter the cavity and combine with TiO_2 during the photocatalytic reaction process. Furthermore, physical and chemical adsorption measurements of CO_2 for single-components revealed that GDY not only exhibits strong CO_2 adsorption capacity but also features a high desorption temperature (Figures S58 and S59, Supporting Information), which is favorable for the

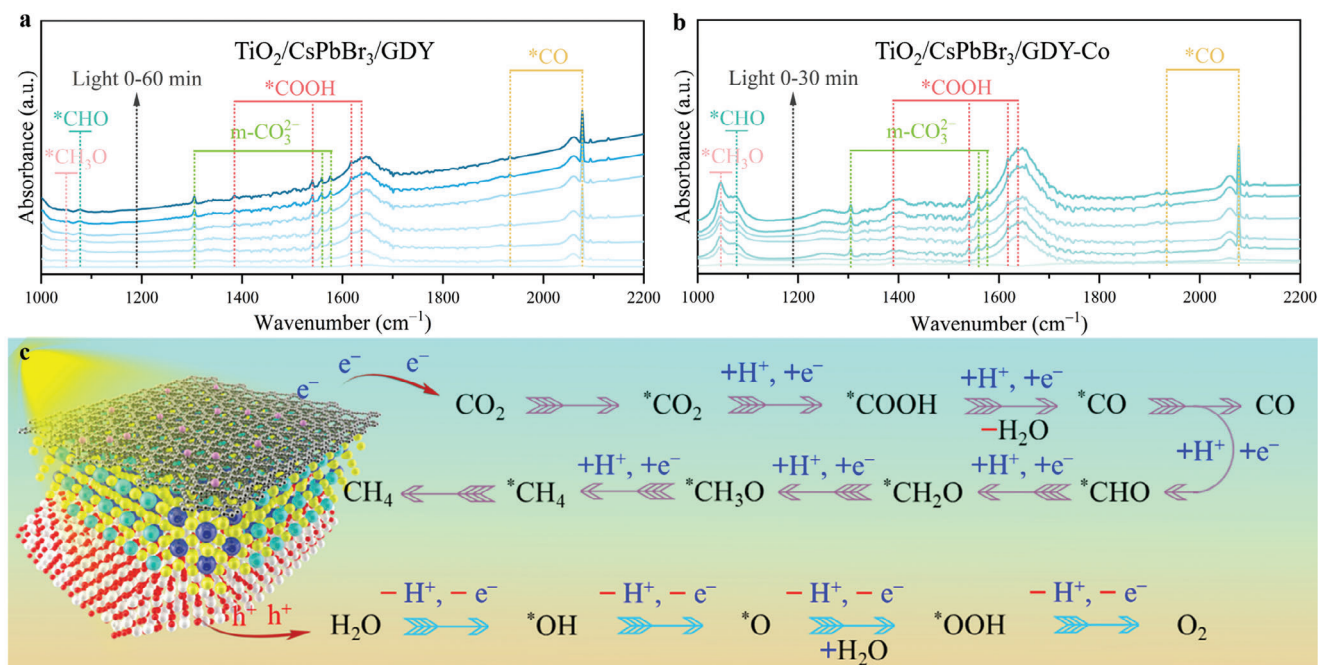


Figure 6. In situ FTIR spectra for photocatalytic CO₂ reduction with a) TiO₂/CsPbBr₃/GDY and b) TiO₂/CsPbBr₃/GDY-Co as photocatalysts. c) The schematic diagram of proposed reaction pathways of photocatalytic CO₂ reduction over TiO₂/CsPbBr₃/GDY-Co.

photocatalytic reduction of CO₂. These results suggest that the photocatalytic stability and activity of TiO₂/MHP/GDY ternary heterojunctions are attributed to the sandwich structures. In these structures, MHPs function as light-harvesting units, while TiO₂ efficiently adsorbs H₂O for water oxidation, and GDY equipped with CO₂ adsorption capacity and hydrophobicity serves as the reduction site. This design can enhance separation efficiency of photogenerated carriers and shield MHPs from direct contact with H₂O, thereby achieving high photocatalytic activity and stability.

To gain a deeper understanding of the origins of products during the photocatalytic process, a series of control experiments were performed using TiO₂/CsPbBr₃/GDY as the photocatalyst (Figure S60, Supporting Information). The absence of light or catalyst led to the absence of detectable presence of products, indicating that the CO₂ reduction process was initiated by light irradiation on the catalyst surface. When CO₂ was substituted with Ar and water was omitted, only trace amounts of CO resulting from the decomposition of residues from sample preparation were detected, initially verifying that the photocatalytic products originated from CO₂ and H₂O. Furthermore, isotope labeling experiments were executed using ¹³CO₂ and H₂¹⁸O as reactants to elucidate the precise origins of products. When ¹³CO₂ was used, mass spectrometry analysis (Figure S61a, Supporting Information) revealed signal peaks attributed to ¹³CH₄ and ¹³CO at *m/z* = 17 and *m/z* = 29, respectively, demonstrating that CO and CH₄ were derived from CO₂ photoreduction. When H₂¹⁸O was employed (Figure S61b, Supporting Information), a signal peak attributed to ¹⁸O₂ emerged at *m/z* = 36, confirming that the stoichiometric amounts of O₂ (Figures S62–S65, Supporting Information) generated during the photocatalytic process indeed originated from water oxidation.

In-situ Fourier transform infrared spectroscopy (in situ FTIR) provides further insight into the reaction mechanism underlying artificial photosynthesis in ternary heterojunction systems. Prior to conducting the formal experiment, the test system was purged with high-purity Ar to eliminate the background interference. Subsequently, CO₂ and water vapor were introduced into the system while the light source was activated. Figure 6a displays the results of an in situ FTIR test using TiO₂/CsPbBr₃/GDY ternary heterojunction as the photocatalyst. As the light exposure time increases, multiple distinct signal peaks gradually emerge within the wavenumber range of 1000–2200 cm⁻¹. Specifically, the signal peaks observed at 1306, 1558, and 1578 cm⁻¹ are indicative of the characteristic vibrations of monodentate carbonate (m-CO₃²⁻).^[53] Prominent characteristic signal peaks detected at 1384, 1539, 1618, and 1636 cm⁻¹ represent *COOH,^[54,55] which is a crucial intermediate during the conversion of CO₂ to CO. Additionally, the presence of *CO intermediates adsorbed on the catalyst surface is confirmed by signal peaks at 1933 and 2077 cm⁻¹.^[56,57] Furthermore, signal peaks at 1048 and 1076 cm⁻¹ correspond to *CH₃O and *CHO, respectively, which are key intermediates in CH₄ formation.^[58] Under the same conditions, further in situ FTIR measurements were conducted on a sample loaded with the cocatalyst Co (TiO₂/CsPbBr₃/GDY-Co). As shown in Figure 6b, the incorporation of the co-catalyst modifies the equilibrium time of the intermediates and the intensities of the peaks, but does not alter the types of intermediates or their characteristic peaks, which indicates that the ternary heterojunction photocatalytic reaction pathway remains unchanged upon the addition of the Co co-catalyst.

Based on the aforementioned results, a fundamental reaction pathway for photocatalytic CO₂ reduction is proposed in Figure 6c, with TiO₂/CsPbBr₃/GDY-Co as an example. Initially,

Table 1. Chemical reagents involved in TiO_2/MO_x preparation process.

Samples	MIL-125- NH_2	Methenamine	Metal salt
$\text{TiO}_2/\text{Bi}_2\text{O}_3$	100 mg	20 mg	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ 150 mg
$\text{TiO}_2/\text{Sb}_2\text{O}_4$	100 mg	10 mg	$\text{Sb}(\text{Ac})_3$ 100 mg

$\text{TiO}_2/\text{CsPbBr}_3/\text{GDY-Co}$ absorbs photons under illumination and generates photogenerated electron-hole pairs. Subsequently, the dual built-in electric field facilitates efficient separation and transport of the photogenerated carriers, resulting in the accumulation of photogenerated electrons primarily in GDY and photogenerated holes mainly in TiO_2 . Ultimately, the photogenerated electrons in the CB of GDY trigger the reduction reaction of CO_2 through a proton-coupled electron transfer (PCET) pathway, progressively generating intermediates $^*\text{COOH}$ and $^*\text{CO}$. The $^*\text{CO}$ intermediate either desorbs to form CO or undergoes further PCET transfer reactions to produce CH_4 . Concurrently, the photogenerated holes in the VB of TiO_2 participate in the oxidation of H_2O to generate O_2 , while also providing the necessary protons for the CO_2 reduction process.

3. Conclusion

In summary, we have successfully demonstrated a versatile strategy that integrates self-templating with in situ sequential deposition to meticulously prepare a series of MHP-based ternary heterojunctions. The innovative sandwich-like hollow structure not only offers dual-sided protection to the MHP photoactive layers but also ensures intimate contact between the reactant substrates and the respective oxidation and reduction catalysts. Moreover, comprehensive characterizations including UPS, XPS, in situ XPS, EPR, transient absorption spectroscopy and photoelectrochemical measurements have unequivocally confirmed that the generation of the dual-interfacial electric field in the ternary heterojunctions can effectively promote the directional separation of photogenerated carriers, with photogenerated electrons and holes accumulating on the reduction and oxidation catalysts, respectively. Consequently, the prepared MHP-based ternary heterojunctions exhibit remarkable photocatalytic stability in water-containing systems for over 200 h, and their photocatalytic activities surpass those of both single perovskites and the corresponding binary heterojunctions by a significant margin. Notably, the CsPbBr_3 -based ternary heterojunction demonstrates an impressive electron consumption rate of up to $1824 \mu\text{mol g}^{-1} \text{h}^{-1}$ for photocatalytic CO_2 reduction coupled with water oxidation, vastly outperforming currently reported halide perovskite-based photocatalysts.

4. Experimental Section

Chemicals: Cesium iodide (CsI , 99.9%) and cesium bromide (CsBr , 99.9%) were purchased from Xi'an Polymer Light Technology Corp. Cesium carbonate (Cs_2CO_3 , 99%) was obtained from J&K. Methanol (99.9%), isopropanol (IPA, 99.5%), ethylene glycol (EG, 98%), acetonitrile (99.8%), titanium isopropoxide ($\text{Ti}(\text{O}^i\text{Pr})_4$, 95%), 2-aminoterephthalic acid ($\text{NH}_2\text{-BDC}$, 98%), silver bromide (AgBr , 98%), copper (I) bromide (CuBr , 99%), copper (I) iodide (CuI , 98%), *N,N*-dimethylformamide

(DMF, 99.5%), tetrabutylammonium hexafluorophosphate (TBAPF₆, 98%), oleic acid (OA, AR), and oleylamine (OAm, AR) were all sourced from Aladdin. Lead acetate trihydrate ($\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$, 99.5%), 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO, 98%), and furfuryl alcohol (99%) were procured from Adamas-beta. Hydriodic acid (HI, 57 wt%), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, AR), and antimony acetate ($\text{Sb}(\text{Ac})_3$, 98%) were procured from Innocem. Bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 99.9%), $^{13}\text{CO}_2$, and H_2^{18}O were obtained from Energy Chemical. Methenamine ($\text{C}_6\text{H}_{12}\text{N}_4$, 99%) was purchased from Sinopharm Chemical Reagent Co. Ltd. Hexakis-[(trimethylsilyl)ethynyl]benzene (HEB-TMS, 97%) was purchased from LEYAN. Hydrobromic acid (HBr, 47%) was purchased from TCI. Cobalt bromide (CoBr_2 , 99.99%) was purchased from Alfa. All chemicals were commercially available and used without further purification.

Preparation of MIL-125- NH_2 : MIL-125- NH_2 was synthesized by modifying the previously reported method.^[59] First, $\text{NH}_2\text{-BDC}$ (840 mg, 4.65 mmol) was dissolved in 60 mL of a mixture of DMF and methanol ($V_{\text{DMF}}:V_{\text{methanol}} = 8:2$) and stirred for 30 min. After the solution turned clear, $\text{Ti}(\text{O}^i\text{Pr})_4$ (900 μL , 3 mmol) was added dropwise and the mixture was stirred for another 10 min. Finally, the resulting mixture was placed into a 100 mL Teflon-lined stainless autoclave and stored at 150 °C for 16 h. After cooling to room temperature, the product was collected by centrifugation, washed with DMF and ethanol, and finally dried to obtain MIL-125- NH_2 .

Preparation of $\text{TiO}_2/\text{PbTiO}_3$: As-prepared MIL-125- NH_2 (100 mg), ethanol (20 mL), EG (5 mL), methenamine (20 mg) and $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$ (100 mg) were first added into a beaker. Subsequently, the mixture was stirred for 10 h at 85 °C in a water bath followed by centrifugation, and the obtained precipitate was washed with deionized water and ethanol. Eventually, the precipitate was annealed at 450 °C for 3 h to get $\text{TiO}_2/\text{PbTiO}_3$. For details on the chemicals used in the preparation of other binary composite materials, refer to Table 1.

Preparation of $\text{TiO}_2/\text{PbTiO}_3/\text{GDY}$ and $\text{TiO}_2/\text{PbTiO}_3/\text{GDY-Co}$: $\text{TiO}_2/\text{PbTiO}_3/\text{GDY}$ was synthesized based on the Glaser-Eglinton coupling reaction reported in the literature.^[34] Typically, $\text{TiO}_2/\text{PbTiO}_3$ (10 mg), CuBr (2 mg), HEB-TMS (2 mg) were first dispersed in DMF (5 mL). After ultrasonic treatment for 10 min, the mixture was stirred at 60 °C for 24 h. Subsequently, the precipitate was collected by centrifugation and further washed with DMF and ethanol to obtain $\text{TiO}_2/\text{PbTiO}_3/\text{GDY}$. Cobalt ions were introduced by adding 0.2 mg of CoBr_2 during the synthesis process. The preparation process for other ternary composite materials ($\text{TiO}_2/\text{Bi}_2\text{O}_3/\text{GDY}$ and $\text{TiO}_2/\text{Sb}_2\text{O}_4/\text{GDY}$) is similar, involving only the substitution of different binary composites.

Preparation of $\text{TiO}_2/\text{CsPbBr}_3/\text{GDY}$ and $\text{TiO}_2/\text{CsPbBr}_3/\text{GDY-Co}$: First, Cs_2CO_3 (200 mg) and OA (30 mL) were added into a round-bottom flask (50 mL), and the mixture was degassed under Ar flow at 140 °C for 1 h before being heated to 180 °C for 30 min to form the Cs-oleate. Second, the obtained Cs-oleate was added into IPA (170 mL) to prepare a Cs-oleate precursor solution (1 mg mL^{-1}). Subsequently, the Cs-oleate precursor solution (4 mL), $\text{TiO}_2/\text{PbTiO}_3/\text{GDY}$ (10 mg), OAm (100 μL), and IPA (1 mL) were added to three-necked round-bottom flask and sonicated for 15 min. Ultimately, HBr (50 μL) was added to the reaction system and stirred for 30 min followed by washing with IPA three times.

Preparation of $\text{TiO}_2/\text{Cs}_3\text{Bi}_2\text{I}_9/\text{GDY}$ and $\text{TiO}_2/\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{GDY}$: First, $\text{TiO}_2/\text{Bi}_2\text{O}_3/\text{GDY}$ (10 mg) and CsI (20 mg) were dispersed in methanol (5 mL) until a uniform dispersion was achieved by sonication. Subsequently, HI (100 μL) was rapidly poured into the above mixture solution under vigorous stirring, and the mixture was continuously stirred for 2 h. Finally, the product was separated by centrifugation and washed with IPA three times. The $\text{TiO}_2/\text{Cs}_3\text{Sb}_2\text{Br}_9/\text{GDY}$ ternary heterojunction was prepared in a similar process, except that CsI and HI are replaced with CsBr (15 mg) and HBr (100 μL), respectively.

Preparation of $\text{TiO}_2/\text{Cs}_2\text{AgBiBr}_6/\text{GDY}$: First, CsBr (18 mg), AgBr (8 mg), methanol (2 mL) and HBr (3 mL) were mixed in a round-bottom flask. The solid reactants were then completely dissolved by ultrasonic treatment. Subsequently, $\text{TiO}_2/\text{Bi}_2\text{O}_3/\text{GDY}$ (10 mg) was introduced into the aforementioned mixture and stirred for 30 min. After the reaction, the precipitate was collected by centrifugation and washed with IPA to obtain the desired $\text{TiO}_2/\text{Cs}_2\text{AgBiBr}_6/\text{GDY}$.

Supporting Information

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

Acknowledgements

This work was financially supported by the National Key R&D Program of China (2022YFA1502902), NSFC (22475152, U21A20286, and 22305214), and the 111 Project of China.

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

CO_2 reduction, metal halide perovskite, photocatalysis, self-template, ternary heterojunction

Received: December 2, 2024

Revised: January 4, 2025

Published online:

- [1] J. Lv, J. Xie, A. G. A. Mohamed, X. Zhang, Y. Feng, L. Jiao, E. Zhou, D. Yuan, Y. Wang, *Nat. Rev. Chem.* **2023**, 7, 91.
- [2] M. Bonchio, J. Bonin, O. Ishitani, T.-B. Lu, T. Morikawa, A. J. Morris, E. Reisner, D. Sarkar, F. M. Toma, M. Robert, *Nat. Catal.* **2023**, 6, 657.
- [3] J. Fu, K. Jiang, X. Qiu, J. Yu, M. Liu, *Mater. Today* **2020**, 32, 222.
- [4] W. Liu, L. Cao, W. Cheng, Y. Cao, X. Liu, W. Zhang, X. Mou, L. Jin, X. Zheng, W. Che, Q. Liu, T. Yao, S. We, *Angew. Chem., Int. Ed.* **2017**, 56, 9312.
- [5] K. Sun, Y. Huang, Q. Wang, W. Zhao, X. Zheng, J. Jiang, H.-L. Jiang, *J. Am. Chem. Soc.* **2024**, 146, 3241.
- [6] J. Wang, H. Zhang, Y. Nian, Y. Chen, H. Cheng, C. Yang, Y. Han, X. Tan, J. Ye, T. Yu, *Adv. Funct. Mater.* **2024**, 34, 2406549.

- [7] F. Li, L. Cheng, J. Fan, Q. Xiang, *J. Mater. Chem. A* **2021**, 9, 23765.
- [8] J. Shamsi, A. S. Urban, M. Imran, L. D. Trizio, L. Manna, *Chem. Rev.* **2019**, 119, 3296.
- [9] Z.-Y. Chen, N.-Y. Huang, Q. Xu, *Coord. Chem. Rev.* **2023**, 481, 215031.
- [10] P. Chen, W.-J. Ong, Z. Shi, N. Li, *Adv. Funct. Mater.* **2020**, 30, 1909667.
- [11] M. L. Davies, *Joule* **2020**, 4, 1626.
- [12] F. Du, X. Liu, J. Liao, D. Yu, N. Zhang, Y. Chen, C. Liang, S. Yang, G. Fang, *Adv. Funct. Mater.* **2024**, 34, 2312175.
- [13] H. Zhao, K. Kordas, S. Ojala, *J. Mater. Chem. A* **2023**, 11, 22656.
- [14] K. Bienkowski, R. Solarska, L. Trinh, J. Wiedera-Kalinowska, B. Al-Anesi, M. Liu, G. K. Grandhi, P. Vivo, B. Oral, B. Yilmaz, R. Yildirim, *ACS Catal.* **2024**, 14, 6603.
- [15] J.-S. Zhao, Y.-F. Mu, L.-Y. Wu, Z.-M. Luo, L. Velasco, M. Sauvan, D. Moonshiram, J.-W. Wang, M. Zhang, T.-B. Lu, *Angew. Chem., Int. Ed.* **2024**, 63, 202401344.
- [16] Y.-F. Mu, H.-L. Liu, M.-R. Zhang, H.-J. Wang, M. Zhang, T.-B. Lu, *J. Energy Chem.* **2023**, 77, 317.
- [17] J. Zhu, L. Zhou, Y. Zhu, J. Huang, L. Hou, J. Shen, S. Dai, C. Li, *Small* **2022**, 18, 2104399.
- [18] J. Gao, X. Qian, Q. Wei, Z. Chen, C. Liu, W. Wang, J. Chen, X. Chen, Y. Liu, G. Wei, *J. Colloid Interface Sci.* **2022**, 623, 974.
- [19] Y.-F. Xu, X.-D. Wang, J.-F. Liao, B.-X. Chen, H.-Y. Chen, D.-B. Kuang, *Adv. Mater. Interfaces* **2018**, 5, 1801015.
- [20] Q.-M. Sun, J.-J. Xu, F.-F. Tao, W. Ye, C. Zhou, J.-H. He, J.-M. Lu, *Angew. Chem., Int. Ed.* **2022**, 61, 202200872.
- [21] L. Ding, F. Bai, B. Borjigin, Y. Li, H. Li, X. Wang, *Chem. Eng. J.* **2022**, 446, 137102.
- [22] L.-Y. Wu, Y.-F. Mu, X.-X. Guo, W. Zhang, Z.-M. Zhang, M. Zhang, T.-B. Lu, *Angew. Chem., Int. Ed.* **2019**, 58, 9491.
- [23] V. Andrei, G. M. Ucoski, C. Pornrungraj, C. Uswachoke, Q. Wang, D. S. Achilleos, H. Kasap, K. P. Sokol, R. A. Jagt, H. Lu, T. Lawson, A. Wagner, S. D. Pike, D. S. Wright, R. L. Z. Hoyer, J. L. MacManus-Driscoll, H. J. Joyce, R. H. Friend, E. Reisner, *Nature* **2022**, 608, 518.
- [24] J. Zhuang, J. Wang, F. Yan, *Nano-Micro Lett.* **2023**, 15, 84.
- [25] Q.-Q. Chu, Z. Sun, D. Wang, B. Cheng, H. Wang, C.-P. Wong, B. Fang, *Matter* **2023**, 6, 3838.
- [26] M. Heydarian, M. Heydarian, P. Schygulla, S. K. Reichmuth, A. J. Bett, J. Hohl-Ebinger, F. Schindler, M. Hermle, M. C. Schubert, P. S. C. Schulze, J. Borchert, S. W. Glunz, *Energy Environ. Sci.* **2024**, 17, 1781.
- [27] Y.-X. Feng, K. Su, Z.-L. Liu, S.-X. Yuan, Y.-F. Mu, M. Zhang, T.-B. Lu, *Appl. Catal. B Environ. Energy* **2024**, 347, 123821.
- [28] B. Kim, W. Lee, S. Lim, *Appl. Surf. Sci.* **2024**, 657, 159829.
- [29] Y. Ma, X. Yi, S. Wang, T. Li, B. Tan, C. Chen, T. Majima, E. R. Waclawik, H. Zhu, J. Wang, *Nat. Commun.* **2022**, 13, 1400.
- [30] J. Zhu, X. F. Lu, D. Luan, X. W. (David) Lou, *Angew. Chem., Int. Ed.* **2024**, 63, 202408846.
- [31] Z.-X. Cai, Z.-L. Wang, J. Kim, Y. Yamauchi, *Adv. Mater.* **2019**, 31, 1804903.
- [32] X. Liu, G. Verma, Z. Chen, B. Hu, Q. Huang, H. Yang, S. Ma, X. Wang, *Innovation* **2022**, 3, 100281.
- [33] Y. Chang, H. Huang, T. Yang, L. Wang, H. Zhu, C. Zhong, *J. Colloid Interface Sci.* **2021**, 599, 785.
- [34] J. Li, X. Han, D. Wang, L. Zhu, M.-H. Ha-Thi, T. Pino, J. Arbiol, L.-Z. Wu, M. N. Ghazzal, *Angew. Chem., Int. Ed.* **2022**, 61, 202210242.
- [35] C. Li, Z. Yu, C. Cui, J. R. Schmidt, D. S. Sholl, R. P. Lively, *J. Phys. Chem. C* **2022**, 126, 21414.
- [36] Z.-W. Wei, H.-J. Wang, C. Zhang, K. Xu, X.-L. Lu, T.-B. Lu, *Angew. Chem., Int. Ed.* **2021**, 60, 16622.
- [37] Y. Feng, M. Xu, H. Liu, W. Li, H. Li, Z. Bian, *Nano Energy* **2020**, 73, 104768.
- [38] H. Lu, Y. Tang, L. Rao, Z. Li, X. Ding, C. Song, B. Yu, *Nanotechnology* **2019**, 30, 295603.
- [39] Z. Hu, K. Li, X. Wu, N. Wang, X. Li, Q. Li, L. Li, K. Lv, *Appl. Catal. B Environ.* **2019**, 256, 117860.

- [40] G. Li, Y. Li, H. Liu, Y. Guo, Y. Li, D. Zhu, *Chem. Commun.* **2010**, 46, 3256.
- [41] F. Tian, Y. Zhang, J. Zhang, C. Pan, *J. Phys. Chem. C* **2012**, 116, 7515.
- [42] H. Chen, A. Guo, J. Zhu, L. Cheng, Q. Wang, *Appl. Surf. Sci.* **2019**, 465, 656.
- [43] K. Su, G.-X. Dong, W. Zhang, Z.-L. Liu, M. Zhang, T.-B. Lu, *ACS Appl. Mater. Interfaces* **2020**, 12, 50464.
- [44] Z. Jiang, W. Wan, H. Li, S. Yuan, H. Zhao, P. K. Wong, *Adv. Mater.* **2018**, 30, 1706108.
- [45] W. Zhang, C.-C. Song, J.-W. Wang, S.-T. Cai, M.-Y. Gao, Y.-X. Feng, T.-B. Lu, *Chin. J. Catal.* **2023**, 52, 176.
- [46] M. Ou, W. Tu, S. Yin, W. Xing, S. Wu, H. Wang, S. Wan, Q. Zhong, R. Xu, *Angew. Chem., Int. Ed.* **2018**, 57, 13570.
- [47] Y.-F. Xu, M.-Z. Yang, B.-X. Chen, X.-D. Wang, H.-Y. Chen, D.-B. Kuang, C.-Y. Su, *J. Am. Chem. Soc.* **2017**, 139, 5660.
- [48] X. Wang, J. He, L. Mao, X. Cai, C. Sun, M. Zhu, *Chem. Eng. J.* **2021**, 416, 128077.
- [49] Y. Jiang, J.-F. Liao, H.-Y. Chen, H.-H. Zhang, J.-Y. Li, X.-D. Wang, D.-B. Kuang, *Chem* **2020**, 6, 766.
- [50] J. Pi, X. Jia, Z. Long, S. Yang, H. Wu, D. Zhou, Q. Wang, H. Zheng, Y. Yang, J. Zhang, J. Qiu, *Adv. Energy Mater.* **2022**, 12, 2202074.
- [51] X. Wang, K. Li, J. He, J. Yang, F. Dong, W. Mai, M. Zhu, *Nano Energy* **2020**, 78, 105388.
- [52] Q. Chen, Y. Ma, L. Wang, X. Lan, J. Shi, *Sol. RRL* **2021**, 5, 2000755.
- [53] Y. Zhang, X. Zhi, J. R. Harmer, H. Xu, K. Davey, J. Ran, S.-Z. Qiao, *Angew. Chem., Int. Ed.* **2022**, 61, 202212355.
- [54] S. Barman, A. Singh, F. A. Rahimi, T. K. Maji, *J. Am. Chem. Soc.* **2021**, 143, 16284.
- [55] G. Zhou, J. Yang, X. Zhu, Q. Li, Q. Yu, W. El-almi, C. Wang, Y. She, J. Qian, H. Xu, H. Li, *J. Energy Chem.* **2020**, 49, 89.
- [56] N. Li, X.-P. Zhai, B. Ma, H.-J. Zhang, M.-J. Xiao, Q. Wang, H.-L. Zhang, *J. Mater. Chem. A* **2023**, 11, 4020.
- [57] Y. Wang, K. Wang, J. Meng, C. Ban, Y. Duan, Y. Feng, S. Jing, J. Ma, D. Yu, L. Gan, X. Zhou, *Nano Energy* **2023**, 109, 108305.
- [58] X. Li, Y. Sun, J. Xu, Y. Shao, J. Wu, X. Xu, Y. Pan, H. Ju, J. Zhu, Y. Xie, *Nat. Energy* **2019**, 4, 690.
- [59] Z. Yang, X. Xu, X. Liang, C. Lei, Y. Cui, W. Wu, Y. Yang, Z. Zhang, Z. Lei, *Appl. Catal. B Environ.* **2017**, 205, 42.