Construction of a ternary WO₃/CsPbBr₃/ZIF-67 heterostructure for enhanced photocatalytic carbon dioxide reduction

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ABSTRACT Using halide perovskite nanomaterials for solar-to-fuel conversion has recently attracted a lot of attention due to their excellent photoelectric properties. However, severe photogenerated charge carrier recombinations and poor reaction kinetics greatly restrict their photocatalytic performance. In this study, a ternary WO₃/CsPbBr₃/ZIF-67 heterostructure was designed for efficient CO₂ photoreduction. The results indicate that the Z-scheme charge transfer pathway constructed between WO₃ and CsPbBr₃ ensures the effective transfer and separation of photogenerated charge carriers. Meanwhile, the subsequent surface modification of zeolitic imidazolate frameworks (ZIF-67) with active Co centers further benefits CO₂ adsorption and activation. Accordingly, the synergistic effects of charge separation and CO₂ uptake greatly promote the photocatalytic activity. The optimal WO₃/CsPbBr₃/ZIF-67 heterostructure yields a CO production of 99.38 μmol g⁻¹ in 3 h, which is 6.8 times of that produced by CsPbBr₃. This work will inspire new insights in developing efficient photocatalysts for CO₂ reduction and even more challenging photocatalytic reactions by elaborately regulating the functional ingredient.

Keywords: Z-scheme heterojunction, halide perovskite, CO₂ photoreduction, heterostructure, charge separation

INTRODUCTION

The ever-increasing shortage of energy supply and worsening of environmental pollution has motivated extensive research interest in the development of sustainable, renewable, and environment-friendly energy [1]. Artificial photosynthesis is one of the most promising energy strategies as it provides a benign pathway to convert CO₂ and H₂O into high-value-added chemicals with the aid of solar energy [2]. However, the photocatalytic CO₂ reduction process requires a strong driving force as the linear molecular structure of CO₂ is thermodynamically stable and is considered the bottleneck step in its catalysis. For improving the total conversion efficiency, researchers have focused on exploring suitable photocatalysts for CO₂ reduction [3–6]. As an emerging photoelectrical material, halide perovskite (PVK) features a high absorption coefficient, wide visible-light absorption, long carrier diffusion length, and a tunable composition. Therefore, it is extensively used in solar cells, photoelectric detection, and light-emitting diodes [7,8]. Recently, it was demonstrated as a suitable photocatalyst for CO₂ reduction.

The new family of PVK nanomaterials provides a new paradigm for photocatalysis [9]. However, the reported photocatalytic performance of single-component PVK catalysts is always unsatisfactory due to their poor CO₂ adsorption ability and serious charge recombination, both of which severely hinder their application in actual photocatalysis [10].

Thus, different engineering strategies have been developed to finely regulate the composition and structure of PVK-based photocatalysts (e.g., element doping, cocatalyst modification, and heterojunction construction). Among them, heterojunction construction accelerates the transfer and separation of the electron-hole pairs and enables the collaboration of different ingredients to improve light harvesting, adsorption of the substrate, and reaction rate. Therefore, it is the most promising strategy for the design of efficient photocatalysts. Consequently, the rational design of PVK-based heterogeneous photocatalysts made by coupling PVK with selected functional materials is of supreme importance to boost their photocatalytic performances [11]. Inspired by this, various PVK-based heterostructures (i.e., CsPbBr₃/g-C₃N₄ [12], CsPbBr₃/Au [13], CsPbBr₃/Bi₂WO₆ [14], and CsPbBr₃/TiO₂ [15]) have been developed, and enhanced CO₂ reduction activity has been achieved. A Z-scheme heterojunction contains a two-photon excitation process, and it maintains the high redox capacity of photocarriers with a high solar energy utilization efficiency [16–18]. In this regard, Z-scheme heterojunctions were recently adopted in the design of PVK-based photocatalysts [19–21]. For example, the authors of this study have illustrated the successful construction of a Z-scheme heterojunction by coupling CsPbBr₃ with an oxide semiconductor (e.g., Fe₂O₃ or Bi₂WO₆) [22,23]. When compared with a single CsPbBr₃, the photocatalytic activity for CO₂ reduction has been largely enhanced, indicating the crucial role of the Z-scheme charge transfer mechanism in both charge separation and charge redox ability. In addition to the construction of the heterojunction, the CO₂ adsorption capacity is another key factor in determining photocatalytic performance, so porous materials such as metal-organic frameworks were applied to promote the CO₂ adsorption and activation of the photocatalysts [24]. Inspired by these efforts, the CO₂ reduction activity of PVK-based Z-scheme photocatalysts could be further improved if the issue of the efficacy of CO₂ adsorption was addressed.

Therefore, aiming at improving both the charge separation and CO₂ adsorption, this study presents a sequential *in situ* growth approach to prepare a WO₃/CsPbBr₃/ZIF-67 (ZIF-67:

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zeolitic imidazolate framework) heterostructure for CO₂ photoreduction. In this ternary system, CsPbBr₃ nanocrystals are loaded on the surface of WO₃ nanosheets (NSs) to construct a Z-scheme heterojunction, providing an efficient transfer pathway for the photogenerated charge carriers. Further modification of ZIF-67 promotes charge separation, and most importantly, improves the CO₂ adsorption and activation simultaneously. The WO₃/CsPbBr₃/ZIF-67 heterostructure displays an obviously enhanced photocatalytic activity toward CO₂ reduction because of the cooperative effects of different functional ingredients.

EXPERIMENTAL SECTION

Preparation of WO₃ nanosheets

The WO₃ NSs were fabricated using a simple hydrothermal procedure as previously reported [25]. The typical procedure was as follows: 2 mol L⁻¹ HCl (12.5 mL) was added dropwise into a 12.5 mL solution containing 6.12 mmol of Na₂WO₄·2H₂O and 1.22 mmol of NH₄F under stirring. Then, 1.53 mmol of oxalic acid was added to the above mixture with the addition of 25 mL deionized H₂O. After stirring for another 30 min, the mixture was transferred to a Teflon autoclave and held at 90°C for 3 h. Next, the as-prepared sample was collected and dried at 70°C. Finally, the WO₃ NSs were obtained *via* an annealing process at 500°C for 1 h.

Preparation of CsPbBr₃ nanocrystal and WO₃/CsPbBr₃ heterostructure

The CsPbBr₃ nanocrystal was synthesized through an antisolvent method [26]. Briefly, a Pb-based precursor was prepared by dissolving 0.55 g of PbBr₂ in a solvent mixture containing 1 mL of propionic acid, 1 mL of butylamine, and 1 mL of isopropanol. Next, 0.43 g of Cs₂CO₃ was dissolved in 3 mL of propionic acid to form the Cs-based precursor. Then, 20 μ L of Cs-based precursor was added to a mixture containing 2 mL of hexene and 1 mL of isopropanol. Subsequently, 100 μ L of Pb-based precursor was quickly added under vigorous stirring. The obtained product was collected using centrifugation, after which it was washed with *n*-hexane and ethyl acetate. Finally, it was dried in a vacuum oven at 70°C.

The WO₃/CsPbBr₃ heterojunction was prepared through a procedure similar to the CsPbBr₃ nanocrystal, except a certain amount of WO₃ NSs (25, 50, and 75 mg) was predispersed in the Cs precursor solution, after which it was treated by ultrasonication for 30 min and stirred for another 3 h to form a uniform suspension.

Preparation of WO₃/CsPbBr₃/ZIF-67 heterostructure

The optimized WO₃/CsPbBr₃ composite (20 mg) was first dispersed into 5 mL of ethyl acetate under vigorous stirring. Next, certain amounts of cobalt acetylacetonate and 2-methylimidazole (2-HMIM) were added to the above mixture and continuously stirred for 1 h. Finally, the product was obtained through centrifugation, washed with ethyl acetate thrice, and dried at 60°C. The molar ratio of cobalt acetylacetonate and 2-HMIM was fixed at 1:4 with the corresponding molar concentration of the two components increasing from 0.5–2 to 1–4 and 2–8 mmol L⁻¹.

Characterization

The crystalline structure of the composite was determined using

X-ray diffraction (XRD, Rigaku Smartlab) using Cu K α radiation at 40 kV and 30 mA. The nanostructure and morphology of the composite were characterized using field emission scanning electron microscopy (FESEM, Hitachi SU8010) and high-resolution transmission electron microscopy (HRTEM, JEOL-2010 HR). The optical absorption behavior of the samples was studied using an ultraviolet-visible (UV-vis) spectrometer (Shimadzu UV-3600). The X-ray photoelectron spectra (XPS) were investigated on a photoelectron spectrometer (ESCALAB 250, Thermo Fisher Scientific). The photoluminescence (PL) spectra were obtained on an Edinburgh FLS980 spectrometer with an excitation wavelength of 400 nm. The CO₂ uptakes were measured on an Autosorb-iQ2-MP instrument. The electron spin resonance (ESR) experiments were tested in toluene/H₂O with the volume ratio of 200:1 for DMPO- $\cdot$ OH and in O₂-saturated toluene for DMPO- $\cdot$ O₂⁻. Transient absorption spectroscopy (TAS) was conducted on a Ti:sapphire laser source (Coherent Legend, 800 nm, 150 fs, 1 kHz repetition rate), and the fs–ns signals were collected using the Helios spectrometers (Ultrafast System LLC). Part of the 800-nm output (75%) pulse was frequency-doubled in a BaSO₄ crystal to form a 350-nm pump light, and the remaining output was concentrated into a sapphire window to generate a white light continuum (420–780 nm). This study used a pump beam with a beam waist of $\sim$ 360 μ m and power intensity of 200 μ J cm⁻².

Photoelectrochemical study

The photoelectrochemical (PEC) characterizations were performed in a three-electrode system. The electrode was prepared using a simple centrifuge method with the same amount of photocatalyst. The as-prepared electrode, Pt foil, and Ag/AgCl were employed as the work, counter, and reference electrodes, respectively. The electrolyte was 0.5 mol L⁻¹ tetrabutylammonium hexafluorophosphate (TBAPF₆) dissolved in ethyl acetate. The electrolyte was purged with N₂ gas to remove the O₂ before the test. The photocurrent responses were tested at a bias of -0.4 V *versus* Ag/AgCl under simulated sunlight irradiation (AM 1.5 G, 100 mW cm⁻²). All PEC characterizations were conducted on a CHI660E electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd.).

Photocatalytic performance study

The photocatalytic reaction was performed in a gas–solid reaction system. First, 5 mg of photocatalyst was dispersed in 1 mL of ethyl acetate and dropped onto a glass substrate. It was then dried at 70°C to remove the organic solvent. Subsequently, the as-prepared photocatalyst film was put in a 40-mL sealed Pyrex bottle filled with CO₂ and H₂O vapor. A 150-W Xe lamp (Zolix) equipped with an AM 1.5 G filter was used as the light source; the light intensity was calibrated to 150 mW cm⁻². The cycling stability of the sample was tested as the reaction atmosphere was refreshed every 2 h by vacuuming and refilling the reactor with CO₂ and H₂O before each cycle.

The yields of the gaseous products were analyzed using a chromatograph (GC9790 Plus, Fuli Analytical Instrument Co., Ltd.) equipped with a flame ionization detector and a thermal conductivity detector. Correspondingly, the total electron consumption yield (Yield_{electron}) of the CO₂ reduction reaction was calculated *via* the following formula: Yield_{electron} = 2Yield_{CO} + 8Yield_{CH₄}. The isotope experiment was conducted with ¹³CO₂ molecules as the isotopic tracer under the same photocatalytic

conditions as mentioned above, and the products were detected using gas chromatography–mass spectrometry (QP2010).

RESULTS AND DISCUSSION

Structure and morphology of the $\text{WO}_3/\text{CsPbBr}_3/\text{ZIF-67}$ heterostructure

The synthetic process of the ternary $\text{WO}_3/\text{CsPbBr}_3/\text{ZIF-67}$ heterostructure is illustrated in Scheme 1. Briefly, the WO_3 NSs were prepared through a hydrothermal procedure followed by a calcination process to remove the crystal H_2O of the $\text{WO}_3\cdot\text{H}_2\text{O}$ precursor. Next, the WO_3 NSs served as nucleation sites for a further anchoring of the CsPbBr_3 nanocrystals *via* the facile antisolvent method. Subsequently, the as-prepared sample was dispersed into the cobalt acetylacetonate and 2-HMIM precursor solution to directly grow the ZIF-67 coating on the surface of the $\text{WO}_3/\text{CsPbBr}_3$.

The phase structures of the samples were investigated using XRD analysis (Fig. S1). The pristine WO_3 NSs showed the characteristic diffraction peaks of the monoclinic phase (JCPDS No. 72-0677). After the antisolvent deposition process, additional diffraction peaks around 15° , 21° , 30° , and 37° emerged, corresponding to the (001), (110), (200), and (211) lattice planes of the CsPbBr_3 (JCPDS No. 18-0364), respectively. In the case of the $\text{WO}_3/\text{CsPbBr}_3/\text{ZIF-67}$ sample, additional characteristic peaks before 10° (due to ZIF-67) appeared, confirming the successful fabrication of the ternary heterostructure.

The morphologies of the as-prepared samples were characterized using SEM and TEM. As shown in Fig. S2 and Fig. 1a, the pristine WO_3 NSs showed a smooth surface with a lateral diameter of ~ 250 nm and a thickness of ~ 25 nm. After the *in situ* loading of the CsPbBr_3 nanocrystals (Fig. 1b), the surface of the

Scheme 1 Schematic illustration of the preparation process of the ternary $\text{WO}_3/\text{CsPbBr}_3/\text{ZIF-67}$ heterostructure.

WO_3 NSs became rough, and particles of ~ 13 nm were distinguished (Fig. S3). After further modification of the ZIF-67, the TEM image revealed that a light shell had formed on the surface of the $\text{WO}_3/\text{CsPbBr}_3$, portrayed using the dotted white line in Fig. 1c. Moreover, the lattice spacings of 0.377 and 0.244 nm can be observed in the HRTEM images (Fig. 1d, e) of the marked area in Fig. 1c, which can be indexed to the (020) facet of monoclinic WO_3 and (211) facet of orthorhombic CsPbBr_3 , respectively. All the corresponding element mappings (Fig. 1f–k and Fig. S4) overlapped well and suggested the successful formation of the $\text{WO}_3/\text{CsPbBr}_3/\text{ZIF-67}$ heterostructure.

The results indicated that the composing proportion and

Figure 1 TEM images of the (a) WO_3 nanosheets, (b) $\text{WO}_3/\text{CsPbBr}_3$ composite, and (c) $\text{WO}_3/\text{CsPbBr}_3/\text{ZIF-67}$ heterostructure; (d, e) HRTEM images of the area marked with a dotted magenta line in (c); and (f–k) corresponding element mapping of the $\text{WO}_3/\text{CsPbBr}_3/\text{ZIF-67}$ heterostructure.

morphology of the ternary $\text{WO}_3/\text{CsPbBr}_3/\text{ZIF-67}$ can be easily tuned by regulating the synthesis conditions. First, the ratio of WO_3 and CsPbBr_3 was changed by adding different amounts of the WO_3 NSs (25, 50, and 75 mg) into the precursor solution of CsPbBr_3 (denoted as $\text{WO}_3(m)/\text{CsPbBr}_3$, $m = 25, 50$, and 75). As displayed in Fig. S1a, all the $\text{WO}_3(m)/\text{CsPbBr}_3$ samples presented a similar XRD pattern, but the diffraction peaks indexed to CsPbBr_3 gradually weakened as the percentage of WO_3 increased. Additionally, it was found that more CsPbBr_3 particles formed on the surface of a single WO_3 nanosheet when less WO_3 was added as the CsPbBr_3 particles tended to aggregate together (Fig. S5). If too much WO_3 was added, only some CsPbBr_3 particles were found on a single WO_3 nanosheet. Therefore, a CsPbBr_3 nanocrystal well-dispersed heterojunction was obtained for the $\text{WO}_3(50)/\text{CsPbBr}_3$ sample (Fig. 1b). Second, the loading amount of the ZIF-67 shell can be regulated by changing the concentration of cobalt acetylacetonate and 2-HMIM (denoted as $\text{WO}_3/\text{CsPbBr}_3/\text{ZIF-67}(x)$, $x = 0.5\text{--}2, 1\text{--}4$, and $2\text{--}8 \text{ mmol L}^{-1}$). Unsurprisingly, the characteristic diffraction peaks of the ZIF-67 gradually intensified as the value of x increased (Fig. S1b), indicating that more ZIF-67 formed at a higher precursor concentration. This is further proven by the TEM images shown in Fig. S6. When the precursor concentration was low ($0.5\text{--}2 \text{ mmol L}^{-1}$), no obvious ZIF-67 shell was observed. However, a higher precursor concentration ($2\text{--}8 \text{ mmol L}^{-1}$) tended to generate individual ZIF-67 nanoparticles rather than a shell, due to the higher homogeneous nucleation possibility of the ZIF-67. Therefore, unless otherwise specified, the $\text{WO}_3/\text{CsPbBr}_3$ and $\text{WO}_3/\text{CsPbBr}_3/\text{ZIF-67}$ composite samples discussed below refer to $\text{WO}_3(50)/\text{CsPbBr}_3$ and

$\text{WO}_3(50)/\text{CsPbBr}_3/\text{ZIF-67}(1\text{--}4)$.

Subsequently, XPS was performed to investigate the surface chemical composition and chemical states of the different samples (Fig. 2 and Fig. S7). Pure CsPbBr_3 nanocrystals synthesized *via* the antisolvent method were also examined. The survey spectra of $\text{WO}_3/\text{CsPbBr}_3/\text{ZIF-67}$ (Fig. 2a) verified the existence of W, O, Pb, Cs, Br, Co, and N, which agreed well with the element mappings. The Co 2p signal (Fig. 2b) can be deconvoluted into two peaks corresponding to Co 2p_{1/2} (796.2 eV) and Co 2p_{3/2} (780.2 eV), both of which were in accordance with those previously reported for ZIF-67 [27,28]. For the W 4f spectra (Fig. 2c), pristine WO_3 NSs exhibited two peaks at the binding energies of 37.57 and 35.44 eV, corresponding to W 4f_{5/2} and W 4f_{7/2}, respectively. These peaks negatively shifted by $\sim 0.12 \text{ eV}$ for $\text{WO}_3/\text{CsPbBr}_3$, and further shifted to lower binding energy (by $\sim 0.16 \text{ eV}$) for $\text{WO}_3/\text{CsPbBr}_3/\text{ZIF-67}$. In contrast, the Pb 4f spectrum of the pristine CsPbBr_3 showed two peaks at the binding energies of 142.89 and 138.02 eV (Fig. 2d), while a positive shift ($\sim 0.20 \text{ eV}$) was observed for $\text{WO}_3/\text{CsPbBr}_3$, and a much higher value was observed ($\sim 0.30 \text{ eV}$) for $\text{WO}_3/\text{CsPbBr}_3/\text{ZIF-67}$. Note that the negative shift in binding energy always suggests the increase in the electron cloud density and *vice versa*. Therefore, these results indicate that the Pb in CsPbBr_3 becomes electron-deficient and the W in WO_3 becomes electron-rich in the composite materials, indicating that a strong interfacial interaction has formed between WO_3 and CsPbBr_3 . Specifically, both the binding energies of W 4f and Pb 4f showed a more obvious shift after the modification of ZIF-67, suggesting that the electron redistribution can be further strengthened due to the intimate contact and

Figure 2 XPS spectra of WO_3 , CsPbBr_3 , $\text{WO}_3/\text{CsPbBr}_3$, and $\text{WO}_3/\text{CsPbBr}_3/\text{ZIF-67}$. Survey spectra of different samples (a); Co 2p of $\text{WO}_3/\text{CsPbBr}_3/\text{ZIF-67}$ (b); W 4f (c), and Pb 4f (d) spectra of different samples.

chemical interaction (e.g., the interaction between the metal ion and surface functional groups) that formed between different components.

Optical and CO₂ adsorption properties of the WO₃/CsPbBr₃/ZIF-67 heterostructure

The optical absorption of all samples was characterized using UV–vis spectroscopy (Fig. 3 and Fig. S8). The pristine WO₃ NSs showed narrow visible-light absorption before 450 nm, and the absorption edge red-shifted to ~537 nm for the WO₃/CsPbBr₃. This can be attributed to the characteristic absorption of the CsPbBr₃ nanocrystals. It was found that the WO₃/CsPbBr₃ samples exhibited nearly the same absorption edge and that the absorption between 400 and 530 nm was slightly reduced as the WO₃ amount increased (Fig. S8a). The absorption located at ~537 nm was like that of WO₃/CsPbBr₃ for the WO₃/CsPbBr₃/ZIF-67 ternary heterostructure. Additionally, a broad shoulder peak presented in the range of 550–670 nm emerged and can be ascribed to the Co³⁺/Co²⁺ redox couple and d–d transition of the Co ion in the ZIF-67 shell [29]. This peak clearly increased with an increase in the loading amount of ZIF-67 (Fig. S8b).

The CO₂ adsorption property is another key factor in both photocatalytic activity and product selectivity [24]; it was evaluated *via* adsorption and desorption tests. Fig. 3b demonstrates that the CO₂ uptake of the WO₃/CsPbBr₃/ZIF-67 heterostructure (18.21 cm³ g^{−1}) was distinctly higher than the uptake of the other samples; it was almost 4.8-fold and 6.1-fold more than that of the pure CsPbBr₃ (3.73 cm³ g^{−1}) and WO₃/CsPbBr₃ (2.98 cm³ g^{−1}) samples. This makes sense as the porous structure of the ZIF-67 is helpful for CO₂ adsorption [30].

Photocatalytic performance for CO₂ reduction

The photocatalytic CO₂ reduction activity of the samples was executed *via* a solid–gas system under simulated sunlight. The dynamic product yields of different samples are shown in Fig. 4a, b. Unsurprisingly, the bare WO₃ showed undetectable activity as its conductive band potential was not negative enough for CO₂ reduction. CO was the main product accompanied by a slight amount of CH₄ for CsPbBr₃, WO₃/CsPbBr₃, and WO₃/CsPbBr₃/ZIF-67. No H₂ or other products were detected, as the solid–gas reaction mode may have suppressed the comparative H₂ generation [22]. The yields of CO and CH₄ linearly increased as the irradiation time became longer. After 3 h of irradiation, the WO₃/CsPbBr₃ presented a CO production of 51.75 μmol g^{−1},

which was 3.6 times that of the bare CsPbBr₃ (14.52 μmol g^{−1}). After additional modification of the ZIF-67, the highest CO yield (99.38 μmol g^{−1}) was achieved at 6.8 times greater than that yielded by CsPbBr₃. These results indicated that the integration of the ternary constituents largely contributed to the enhanced photocatalytic CO₂ reduction performances. Additionally, all the samples exhibited a higher yield of CO over CH₄, of which the underlining mechanism is not currently clear. According to previous reports, it can be tentatively speculated that the different surface chemical states of PVK resulted from different syntheses, post-treatment processes, and catalytic conditions and that these differences may affect the product selectivity. However, further investigation is needed.

The results also indicated that the composition of the heterostructures had a big impact on their catalytic performance. As shown in Fig. 4c, as expected, all heterostructures exhibited higher activity than the two pristine counterparts. The product yields first increased as the amount of WO₃ NSs increased from 25 to 50 mg. The highest electron yield of 120.46 μmol g^{−1} was obtained for WO₃(50)/CsPbBr₃. However, this value decreased as the amount of WO₃ NSs continued to increase, likely because excess WO₃ NSs would hamper the utilization of incident light due to less visible-light harvesting ability. The same phenomenon was observed in the case of the WO₃/CsPbBr₃/ZIF-67 heterostructure; a maximum electron yield of 210.67 μmol g^{−1} was achieved for the WO₃/CsPbBr₃/ZIF-67(1–4) sample. These results verified that an appropriate percentage of the three components was crucial for photocatalytic performance. The underlying mechanism will be discussed in detail later.

Apart from photoactivity, photostability was an important factor in the evaluation of the photocatalyst. Therefore, five consecutive runs of catalytic experiments were performed on the ternary WO₃/CsPbBr₃/ZIF-67 heterostructure. As shown in Fig. S9, no obvious activity or phase structure changes were found after the stability tests. This can be attributed to the hydrophobic ZIF coating that could protect CsPbBr₃ from contact with H₂O molecules. Finally, to validate the carbon source of the reaction products, a ¹³C-labeled isotopic trace experiment was conducted by replacing ¹²CO₂ with ¹³CO₂. As shown in Fig. S10, signals with the mass-to-charge ratio (*m/z*) value of 29 and 45 (ascribed to ¹³CO and ¹³CO₂) can be detected, demonstrating the fact that the reductive products were generated from the photocatalytic CO₂ reduction reaction. It should be noted that the signal of ¹³CH₄ was too weak to be detected, indicating that the yield was

Figure 3 (a) UV–vis spectra and (b) CO₂ adsorption/desorption isotherms at 298 K of the WO₃, WO₃/CsPbBr₃, and WO₃/CsPbBr₃/ZIF-67 heterostructures.

Figure 4 Photocatalytic yield–time courses of the samples: (a) CO and (b) CH_4 . (c) Comparison of the total product and electron yields of the different samples after 3-h light irradiation (AM 1.5 G, 150 mW cm^{-2}).

too low.

Photocatalytic mechanism analysis

The charge transfer and transport kinetics of the samples were investigated in detail to evaluate the underlying reason for the enhanced CO_2 photoreduction performance of the $\text{WO}_3/\text{CsPbBr}_3/\text{ZIF-67}$ nanocomposite and possible photocatalytic mechanism. According to the UV–vis spectra and Mott–Schottky plots (Fig. S11), the bandgap and flatband potential (quasi-Fermi level) of the WO_3 NSs were determined as 2.64 and 0.42 V, respectively, *versus* normal hydrogen electrode (NHE). Therefore, the conduction band minimum (CBM) and valence band maximum (VBM) of the WO_3 NSs were calculated as ~ 0.32 and ~ 2.96 V *versus* NHE, respectively [31]. The CsPbBr_3 nanocrystals typically show a CBM and VBM of -0.90 and 1.50 V *versus* NHE, respectively, as the authors' previous report [8]. Therefore, a staggering energy band arrangement is formed between WO_3 and CsPbBr_3 , facilitating the faster transfer of the photogenerated charge carriers.

The ESR measurement was performed with 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) as the spin trap agent to investigate the $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ species to further confirm the actual charge transfer route (type-II or Z-scheme) at the interface. As illustrated in Fig. 5a, four characteristic peaks with the intensity ratio approximated to 1:1:1:1 for the DMPO- $\cdot\text{O}_2^-$ adducts were observed for CsPbBr_3 and $\text{WO}_3/\text{CsPbBr}_3$; however, no signals were detected for the pristine WO_3 since its conductive band edge was too positive to generate $\cdot\text{O}_2^-$ ($\text{O}_2/\cdot\text{O}_2^- = -0.33$ V *versus*

NHE) [32]. For detecting $\cdot\text{OH}$, the bare CsPbBr_3 did not show any detectable signals as its valence band (VB) potential was more negative than the $\cdot\text{OH}/\text{H}_2\text{O}$ ($\cdot\text{OH}/\text{H}_2\text{O} = 2.40$ V *versus* NHE) [33]. Nevertheless, both WO_3 and $\text{WO}_3/\text{CsPbBr}_3$ presented obvious peaks with the intensity ratio of $\sim 1:2:2:1$ (Fig. 5b) that can be assigned to the characteristic signal of the DMPO- $\cdot\text{OH}$ adducts.

In contrast, given that the $\text{WO}_3/\text{CsPbBr}_3$ composite followed a traditional type-II charge transfer pathway (Fig. 5c), photoelectrons accumulated on the conduction band (CB) of the WO_3 , and holes accumulated on the VB of the CsPbBr_3 . Therefore, no signals of $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ were detected for the $\text{WO}_3/\text{CsPbBr}_3$ sample. Apparently, this hypothesis was mutually exclusive with the obtained ESR data that provided solid evidence for the construction of a Z-scheme charge transfer path between WO_3 and CsPbBr_3 rather than a type-II heterojunction due to the preservation of strong oxidation and reduction ability of the WO_3 and the CsPbBr_3 , respectively. Such a Z-scheme heterojunction would result in a fast charge transfer and separation that should contribute to the enhanced photocatalytic performance for CO_2 reduction.

The steady-state and transient PL measurements were performed to further shed light on the charge transfer property. As shown in Fig. 6a, under an excitation of 408-nm monochromatic light, the pristine WO_3 NSs did not show detectable PL signals, while the pure CsPbBr_3 nanocrystal presented a broad PL emission with the maximum absorption wavelength (λ_{max}) at 519 nm. This signal was clearly reduced for $\text{WO}_3/\text{CsPbBr}_3$,

Figure 5 Electron spin resonance spectra of (a) DMPO- $\cdot\text{O}_2^-$ and (b) DMPO- $\cdot\text{OH}$ of CsPbBr_3 , WO_3 , and $\text{WO}_3/\text{CsPbBr}_3$; the (c) diagram of the possible charge transfer mechanism for type-II and Z-scheme heterojunctions.

indicating the enhanced charge extraction and effective suppression of the radiative recombination of photogenerated electron-hole pairs in CsPbBr_3 [34]. Interestingly, the results indicated that the PL intensity was almost quenched for the $\text{WO}_3/\text{CsPbBr}_3/\text{ZIF-67}$ heterostructure, demonstrating that the introduction of ZIF-67 further promotes the extraction of photogenerated electrons. ZIF-67, with an active Co center, has been frequently reported as a cocatalyst in photocatalytic CO_2 reduction reactions; it was believed that the Co center was conducive to charge extraction [30,35,36]. The PL decay of the as-prepared samples was monitored at 519 nm and fitted with a bi-exponential function model (Fig. 6b and Table S1). All the samples presented a rapid decay in the nanosecond scale; the average lifetimes largely decreased from 29.33 (CsPbBr_3) to 9.53 ($\text{WO}_3/\text{CsPbBr}_3$) and 4.48 ns ($\text{WO}_3/\text{CsPbBr}_3/\text{ZIF-67}$). This trend agreed well with the digital photographs taken under 365-nm ultraviolet radiation (Fig. S12), indicating that the construction of binary and ternary heterostructures provided fast charge transfer pathways for the photogenerated charge carriers. Next, photocurrent response measurements were performed. As demonstrated in Fig. 6c, all the samples presented a repeatable response to a “light on-off” state at -0.4 V versus Ag/AgCl. Among them, the photocurrent densities of both heterostructure catalysts were obviously enhanced, and the ternary $\text{WO}_3/\text{CsPbBr}_3/\text{ZIF-67}$ heterostructure exhibited the highest value.

These results indicated that the construction of the heterostructure was beneficial to this process as photocurrents were generated primarily by the transfer and separation of the photogenerated carriers [37,38].

This study utilized ultrafast TAS to deeply clarify the enhanced interfacial charge transfer process in the $\text{WO}_3/\text{CsPbBr}_3/\text{ZIF-67}$ heterostructure. When pumped at 355 nm, both the pristine CsPbBr_3 nanocrystals and composites exhibited a negative broadband single in the range of 430–650 nm, with a maximum peak at ~ 517 nm (Fig. 7a–c), which was assigned to the ground-state bleaching signal of CsPbBr_3 [13,39,40]. The pure WO_3 did not show a detectable signal under the same test conditions [41]. Clearly, the intensities of the bleaching peaks of both nanocomposites were lower than the bleaching peak of CsPbBr_3 at the same delay time. The average recovery lifetime (τ_{average}) of bare CsPbBr_3 was calculated to be 5311.25 ps by monitoring the signal intensity changes at 517 nm (Fig. 7d and Table S2). This dramatically decreased to 1586.35 ps for $\text{WO}_3/\text{CsPbBr}_3$ and 531.44 ps for $\text{WO}_3/\text{CsPbBr}_3/\text{ZIF-67}$. The faster recovery rate of the bleaching signal indicated that the radiative recombination of the photocarriers of CsPbBr_3 was effectively inhibited. This result, along with the abovementioned transient PL and photocurrent results, confirmed that the rational integration of CsPbBr_3 with WO_3 and ZIF-67 benefited both the charge transfer and separation [23].

Figure 6 (a) Steady-state and (b) transient photoluminescence spectra of the samples excited at 408 nm; (c) chopped photocurrent response at a bias of -0.4 V versus Ag/AgCl under simulated sunlight irradiation of AM 1.5 G, 100 mW cm^{-2} ; (d) schematic photocatalytic mechanism of the $\text{WO}_3/\text{CsPbBr}_3/\text{ZIF-67}$ heterostructure.

Figure 7 TAS recorded at different time delays, up to 1 ns, for (a) CsPbBr_3 , (b) $\text{WO}_3/\text{CsPbBr}_3$, and (c) $\text{WO}_3/\text{CsPbBr}_3/\text{ZIF-67}$; (d) the corresponding dynamic curves at 517 nm of the different samples upon 355 nm ($200\text{ }\mu\text{J cm}^{-2}$, 1000 Hz).

Finally, a possible photocatalytic mechanism for the reduction of CO₂ with the WO₃/CsPbBr₃/ZIF-67 heterostructure was tentatively proposed (Fig. 6d). WO₃ and CsPbBr₃ were excited to generate electrons and holes under light irradiation. The photoelectrons in the CB of WO₃ transferred to recombine with the photoinduced holes in the VB of CsPbBr₃ due to the construction of the Z-scheme heterojunction, leading to the spatial separation of the photogenerated electron-hole pairs. Consequently, the electrons gathered in the CB of CsPbBr₃ subsequently migrated to the Co center of the ZIF-67 shell and reacted with the CO₂ molecule adsorbed in the porous skeleton. Meanwhile, the holes that accumulated on the VB of WO₃ were quickly quenched by H₂O to generate O₂. The photocatalytic activity for CO₂ reduction was greatly improved compared with the individual counterpart due to the synergistic effect of superior CO₂ adsorption and charge separation in the multi-component heterostructure.

CONCLUSIONS

In this study, we successfully synthesized a new WO₃/CsPbBr₃/ZIF-67 heterostructure for the photocatalytic reduction of CO₂ through a two-step solution route. A 6.8-fold enhancement in CO production was obtained compared with that of single CsPbBr₃ by rationally regulating the composition of the ternary heterostructure. Detailed characterizations confirmed the successful construction of the Z-scheme heterojunction between WO₃ and CsPbBr₃ and its accelerated charge transfer and separation. Additionally, the coating of ZIF-67 further sped up the charge separation and improved the CO₂ adsorption. The combinative effect of the Z-scheme heterojunction and satisfactory CO₂ adsorption property led to more effective electron-hole separation and photocatalytic activity. This study provides a meaningful guide for developing new types of halide perovskite-based photocatalysts for various photocatalysis applications. Additionally, this approach can be extended to lead-free halide perovskite or other metal halide materials.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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构建三元WO₃/CsPbBr₃/ZIF-67异质结用于高效光催化CO₂还原

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摘要 近年来, 卤素钙钛矿纳米材料以其优异的光电性能在光催化等领域引起了关注. 然而, 光生载流子严重的复合反应和较差的反应动力学也极大地限制了其光催化性能. 本论文设计合成了一种三元WO₃/CsPbBr₃/ZIF-67异质光催化剂, 并将其应用于有效的CO₂光还原反应. 研究表明, WO₃与CsPbBr₃之间构建的Z型电荷转移路径能够保证光生载流子的有效转移和分离. 此外, 在表面修饰具有活性Co中心的ZIF-67壳层作为助催化剂有利于改善复合材料的CO₂的吸附和活化能力. 因此, 电荷分离和CO₂吸附性能的增强大大提高了WO₃/CsPbBr₃/ZIF-67的光催化活性, 还原产物中CO产率达到99.38 μmol g⁻¹, 是单一CsPbBr₃的6.8倍. 这项工作有望为开发高效的卤素钙钛矿基光催化剂及其在CO₂还原和其他复杂光催化反应中的应用提供参考.