


 Cite this: *Chem. Commun.*, 2024, 60, 8900

 Received 6th June 2024,
Accepted 20th July 2024

DOI: 10.1039/d4cc02753a

rsc.li/chemcomm

Enhanced CO₂ conversion in dielectric barrier discharge plasma coupled with a heterojunction photocatalyst†

 Xiao Feng,^a Lefei Cao,^b Chengfan Fu,^b Fei Qi,^{*b} Nan Zhang,^b Yayun Pu,^b Zhiyu Liang,^b Xiaosheng Tang^{ib} ^{*ab} and Qiang Huang^{ib} ^{*b}

CsPbBr₃ quantum dots were grown on ReS₂ nanosheets to form CsPbBr₃@ReS₂ heterojunctions using an anti-solvent method. The composition, morphology, spatial distribution, and optical absorption of samples were characterized. CsPbBr₃@ReS₂-15 exhibits not only a higher photocatalytic performance than CsPbBr₃ due to the improved optical absorption and Z-scheme charge migration, but also a higher CO₂ conversion ratio (35.60%) and energy efficiency (13.10%) in the dielectric barrier discharge (DBD) plasma due to superior photocatalytic activity, increased micro-discharge time, and improved discharge uniformity. This work provides a strategy for plasma photocatalytic CO₂ conversion.

Conversion of CO₂ into high value-added chemicals and fuels *via* renewable green electricity is becoming increasingly pressing because promising potential exists to resolve the greenhouse effect and energy crisis problems.^{1,2} CO₂ molecules are inert and possess ultra-high thermal stability, requiring the energy of 750 kJ mol⁻¹ to disintegrate the carbon–oxygen double bond, which leads to significant challenges for the traditional thermal approach to CO₂ decomposition.³ Non-thermal plasma (NTP) is considered a promising alternative for reducing CO₂ gases into syngas or other valuable chemicals at mild temperatures.⁴ At present, various NTP methods have been proven to convert CO₂ into CO, including dielectric barrier discharge (DBD),⁵ corona discharge,⁶ glow discharge,⁷ microwave discharge,⁸ gliding arc,⁹ and radio-frequency plasma.¹⁰ It is advantageous to use DBD plasma because it is affordable, and it can produce a high electron density. Thus far, DBD plasma has been widely used for CO₂ conversion, and previous reports indicate that packing materials in the DBD plasma reactor can increase the CO₂ conversion efficiency.⁶ In fact, during CO₂ conversion *via* the DBD

plasma approach, there are many high-energy electrons and ultraviolet-visible photons that can stimulate the photocatalysis process. Therefore, it is significant to exploit suitable photocatalysts as packing materials to enhance the CO₂ conversion efficiency for DBD plasma.

There has recently been great interest in halide perovskites, such as CsPbBr₃, in photocatalytic fields due to their wide range of visible light absorption and high absorption coefficient.¹¹ However, the low separation and high recombination rate of photoexcited carriers leads to low CO₂ conversion efficiency for CsPbBr₃.¹² Fortunately, the construction of a heterojunction is proposed to break through these issues. The combination of CsPbBr₃ with two-dimensional (2D) semiconductors to form a heterojunction is a potential strategy to increase the CO₂ photoreduction efficiency, because 2D semiconductors usually have a large specific area, abundant active sites, and short distance of charge transportation.

ReS₂, one member of 2D semiconductors, presents the outstanding optoelectronic properties of direct bandgap, strong optical absorption, and ultra-high optical responsivity. Therefore, it is meaningful to build a heterojunction of CsPbBr₃ and ReS₂ to increase the CO₂ photoreduction efficiency. Additionally, it is also beneficial to prepare a porous heterostructure of CsPbBr₃ and ReS₂. The porous structure has the advantages of a large specific surface area and abundant surface topographies to increase the CO₂ photoreduction.¹³ The porous photocatalysts in DBD plasma can create micro-discharges in the pores, which in turn change the local electric field strength and discharge type of the plasma, affecting CO₂ conversion reactions. Porous surfaces can adsorb active excited species generated during the plasma discharge, thus increasing the residence time of active species and facilitating surface catalytic reactions.¹⁴ To the best of our knowledge, the construction of a CsPbBr₃@ReS₂ heterojunction with a porous surface structure has not been previously reported.

In this work, CsPbBr₃ quantum dots (QDs) were grown *in situ* on porous ReS₂ microspheres to form a CsPbBr₃@ReS₂ heterojunction. Due to the increased optical absorption and enhanced separation of photogenerated carriers, the CO₂

^a State Key Laboratory of Power Transmission Equipment Technology, Chongqing University, Chongqing 400044, China. E-mail: xstang@cqu.edu.cn

^b School of Optoelectronic Engineering, Chongqing University of Posts and Telecommunications, Chongqing 400065, China.
E-mail: huangqiang@cqupt.edu.cn, qifei@cqupt.edu.cn

† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d4cc02753a>

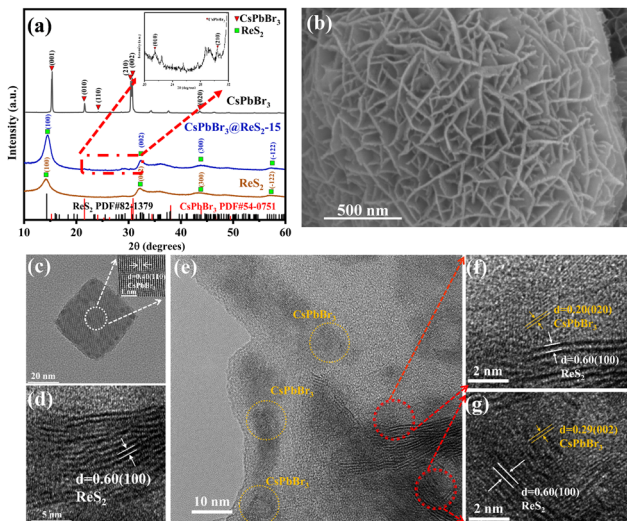


Fig. 1 (a) XRD patterns of CsPbBr₃, ReS₂, and CsPbBr₃@ReS₂. (b) SEM image of ReS₂; HRTEM images of (c) CsPbBr₃, (d) ReS₂, and (e)–(g) CsPbBr₃@ReS₂. The inset in (c) shows an enlarged HRTEM image of CsPbBr₃.

photoreduction efficiency of CsPbBr₃@ReS₂ is higher than that of pristine CsPbBr₃. CsPbBr₃@ReS₂ heterojunction photocatalysts were used to increase the CO₂ conversion ratio and energy efficiency in DBD plasma, which benefitted from the synergistic conversion of CO₂ by the DBD plasma and heterojunction photocatalyst. This work provides guidance for future designs of plasma photocatalytic systems for efficient CO₂ conversion.

The sample preparation details are shown in the Experimental section (ESI[†]). Fig. 1a shows the X-ray diffraction (XRD) patterns of CsPbBr₃, ReS₂, and CsPbBr₃@ReS₂-15. The XRD peaks of CsPbBr₃ QDs at 15.3°, 21.6°, 24.1°, 30.4°, 30.7°, and 43.6° were attributed to the (001), (010), (110), (210), (002), and (020) planes, respectively, and were consistent with the standard card PDF #54-0751. XRD peaks corresponding to the (100), (002), (300), and (−122) planes were detected for ReS₂ microspheres. Obvious XRD peaks for ReS₂ were observed for CsPbBr₃@ReS₂-15, while weak XRD peak signals at 21.6° and 30.4° belonging to the (010) and (210) planes of CsPbBr₃ were also detected, which were due to the low content and small size of CsPbBr₃. A scanning electron microscopy (SEM) image of prepared ReS₂ revealed a microsphere structure (Fig. 1b). Additionally, there were many flakes and holes on the microsphere surface, which are favorable for anchoring CsPbBr₃ QDs and absorbing CO₂ molecules.

In the high-resolution transmission electron microscopy (HRTEM) image in Fig. 1c, the CsPbBr₃ QDs exhibited a cubic shape and lattice spacing of 0.40 nm. The ReS₂ flake in Fig. 1d presents a few layers with a lattice distance of 0.60 nm corresponding to the (100) plane. Fig. 1e shows that CsPbBr₃ QDs are anchored on the ReS₂ surface for CsPbBr₃@ReS₂-15. Compared with the pristine CsPbBr₃ QDs, the size of CsPbBr₃ QDs on ReS₂ decreases, and the corresponding shape changes into an irregular structure, which may induce more catalytic active sites because of a higher surface volume ratio. Fig. 1f and g shows the HRTEM images corresponding to the red circle regions in Fig. 1e. It is observed that the (020) plane with a lattice spacing of 0.2 nm and the (002) plane with a lattice spacing of 0.29 nm for CsPbBr₃ adjoin the (100) plane

with a lattice spacing of 0.60 nm for ReS₂, verifying the formation of a CsPbBr₃@ReS₂ heterojunction. In addition, the energy dispersive spectroscopy (EDS) elemental mapping (Fig. S1, ESI[†]) shows that there is adequate overlap of Cs, Pb, Br, Re, and S elements.

The surface chemical states and interfacial interactions were investigated by X-ray photoelectron spectroscopy (XPS) analysis. The XPS full spectrum (Fig. 2a) verified the presence of Cs, Pb, Br, Re, and S elements in CsPbBr₃@ReS₂-15. Compared to the pristine CsPbBr₃, the Cs 3d spectrum of CsPbBr₃@ReS₂-15 (Fig. 2b) exhibited two XPS peaks at 737.79 and 723.82 eV corresponding to Cs 3d_{3/2} and Cs 3d_{5/2}, respectively, which were not significantly shifted. However, the Pb 4f (Fig. 2c) and Br 3d (Fig. 2d) binding energies were redshifted by 1.20 and 0.23 eV, respectively. In contrast, the Re 4f (Fig. 2e) and S 2p (Fig. 2f) binding energies of CsPbBr₃@ReS₂-15 showed the opposite trend, whereby the Re 4f and S 2p peaks were blueshifted by 1.00 and 0.68 eV, respectively. A higher electron binding energy indicates a decrease in electron density, while a lower electron binding energy indicates an increase in electron density. Consequently, the XPS results denote electron transfer from ReS₂ to CsPbBr₃ within the CsPbBr₃@ReS₂ heterojunction, indicating the intimate interfacial contact and robust chemical interaction between CsPbBr₃ and ReS₂. Fig. S2 (ESI[†]) shows that CsPbBr₃@ReS₂ has a lower photoluminescence (PL) intensity than that of CsPbBr₃, demonstrating the increased separation of photogenerated carriers due to the heterojunction.

To obtain the band structure, UV-vis spectra and valence band (VB) XPS spectra were obtained. The optical absorption edges of pristine CsPbBr₃ and ReS₂ are about 544 and 805 nm in Fig. S3a (ESI[†]), respectively, suggesting their wide light absorption range. According to the inset in Fig. S3a (ESI[†]), the optical absorption ability of CsPbBr₃@ReS₂-15 is stronger compared to CsPbBr₃ and ReS₂, which may be due to the strong electron coupling between CsPbBr₃ and ReS₂, indicating the promising capacity of solar light utilization. In addition, Fig. S3b (ESI[†]) presents the Tauc plots of CsPbBr₃ and ReS₂, from which the bandgap energy (E_g) of 2.30 and 1.57 eV was determined for CsPbBr₃ and ReS₂, respectively. Meanwhile, the VB positions of CsPbBr₃ and ReS₂ are respectively confirmed to be 1.03 and 1.25 eV, as shown in Fig. S4 (ESI[†]). Then, the conduction band (CB) positions ($E_g = CB - VB$) of CsPbBr₃ and ReS₂ are calculated to be −1.27 eV and −0.32 eV, respectively.

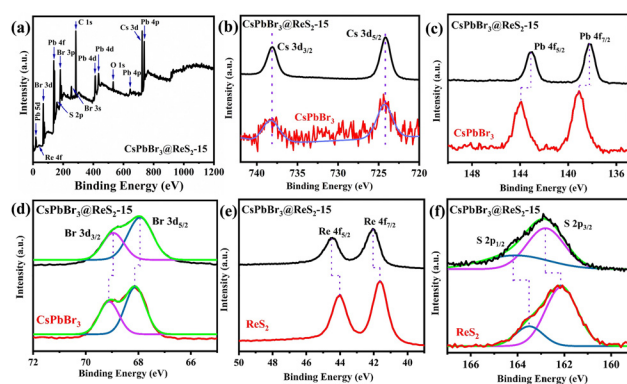


Fig. 2 (a) XPS full spectrum of CsPbBr₃@ReS₂-15. High-resolution XPS spectra of (b) Cs 3d, (c) Pb 4f, and (d) Br 3d of (e) Re 4f and (f) S 2p.

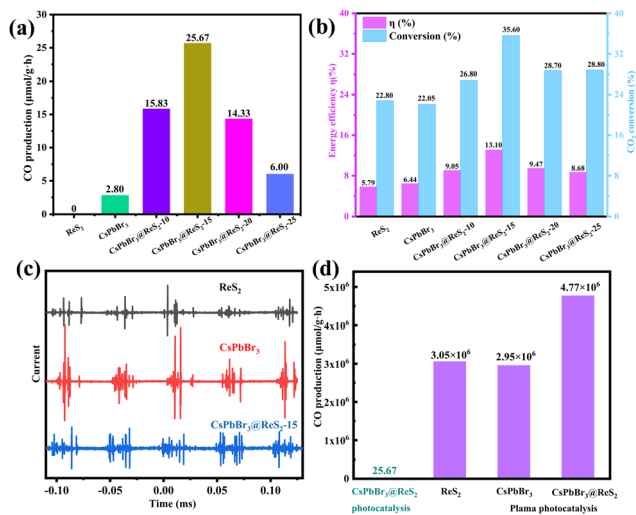


Fig. 3 (a) Photocatalysis, (b) plasma photocatalysis performances, and (c) discharge current of ReS₂, CsPbBr₃, and CsPbBr₃@ReS₂; (d) CO yield of CsPbBr₃@ReS₂ photocatalysis, ReS₂ plasma catalysis, and plasma photocatalysis of CsPbBr₃ and CsPbBr₃@ReS₂.

Especially, it is noted that the band structure of ReS₂ does not match with the reduction potential (−0.52 V) of CO₂ conversion to CO, which agrees with the result of the CO₂ photoreduction for ReS₂ in Fig. 3a. However, the band alignment of the CsPbBr₃@ReS₂ heterojunction meets the requirements for CO₂ conversion to CO, as shown in Fig. S3c (ESI[†]). CsPbBr₃@ReS₂ presents increased photocatalytic efficiency of CO₂ reduction as compared to that of CsPbBr₃ and ReS₂ in Fig. 3a. The traditional type II heterojunction mechanism cannot reasonably explain the principle of charge carrier transfer and photocatalytic CO₂ reduction for CsPbBr₃@ReS₂-15. Therefore, a Z-type charge flow path is proposed for CsPbBr₃@ReS₂-15. As a result, the photogenerated carrier separation efficiency of ReS₂ and CsPbBr₃ in the heterostructure is enhanced, improving the CO₂ photoreduction performance.^{15,16} Additionally, the main CO₂ photoreduction processes for CsPbBr₃@ReS₂ are summarized as reaction Formulas S1–S4 (ESI[†]).

To examine the photocatalytic performance of samples, the products of CO₂ photoreduction were tested. In Fig. 3a, after 3 h of continuous light irradiation, all samples showed 100% selectivity for CO, while CsPbBr₃ possessed low activity (CO yield = 2.80 μmol g^{−1} h^{−1}). Additionally, ReS₂ does not show CO₂ photoreduction ability, which is consistent with the band arrangement structure of ReS₂. However, when CsPbBr₃ is anchored on ReS₂, the CO₂ photoreduction performance is greatly enhanced. Particularly, the largest CO yield (25.67 μmol g^{−1} h^{−1}) was for CsPbBr₃@ReS₂-15, and was 9.17-fold higher than that of CsPbBr₃ (2.80 μmol g^{−1} h^{−1}). Because coupling with ReS₂ had a significant role in the photocatalytic performance of CsPbBr₃, the effects of the molar ratio of CsPbBr₃ to ReS₂ in the heterojunction on the photocatalytic activity were further investigated. Compared to CsPbBr₃@ReS₂-15 (25.67 μmol g^{−1} h^{−1}), the CO production of CsPbBr₃@ReS₂-20 (14.33 μmol g^{−1} h^{−1}) and CsPbBr₃@ReS₂-25 (6.00 μmol g^{−1} h^{−1}) clearly decreased, which occurred because the excess ReS₂ impeded effective utilization of the photon energy due to a lack of photocatalytic activity for CO₂ reduction by pristine ReS₂.

In DBD plasma, electrons are subjected to an applied electric field and gain sufficient energy to obtain high velocity. Afterwards, the high-energy electrons collide with the gas molecules in the discharge gap, resulting in gas ionization, which triggers an electron avalanche.¹⁷ In addition to elastic collisions, inelastic collisions also occur in the plasma to produce many active species, which can be involved in a range of chemical reactions. More importantly, CO₂ molecules can be activated and enter into vibrationally excited states CO₂V* in plasma to decrease the reaction barrier to CO₂ reduction.¹⁸ Therefore, it is significant to employ the active state CO₂V* in DBD plasma to induce photocatalytic CO₂ conversion.

The plasma photocatalytic CO₂ reduction performances for ReS₂, CsPbBr₃, and CsPbBr₃@ReS₂ with different molar ratios are shown in Fig. 3b, and the test details are described in the ESI.[†] It is found that the plasma photocatalytic performance of CsPbBr₃@ReS₂ is higher than that of ReS₂ and CsPbBr₃. CsPbBr₃@ReS₂-15 exhibits the highest CO₂ conversion (35.60%) and energy efficiency (13.10%), which is attributed to the optimal photocatalytic activity, as shown in Fig. 3a. Moreover, the porous surface structure of ReS₂ results in increased residence time of CO₂ molecules in the reaction region¹⁹ and increases the chance of collisions between electrons and CO₂. This explains the higher CO₂ conversion in DBD plasma filled with ReS₂ (22.80%) compared to CsPbBr₃ (22.05%). In contrast, the energy efficiency of the plasma filled with ReS₂ was slightly lower than that of the plasma filled with CsPbBr₃, which may be due to the higher energy input per CO₂ molecule, resulting in a decreasing trend in energy utilization efficiency.²⁰

The reasons for performance differences were further explored by measuring the discharge characteristics and charge properties of DBD plasma. The total current consists of both conduction current and displacement current. Conduction current is formed by the directional movement of charged particles in the plasma under the influence of an electric field. The charge characteristics such as lifetime and discharge intensity can be determined by conduction current. In fact, filling the DBD plasma with catalyst is expected to reduce the amplitude of the current peak and cause a change in the discharge modes. Usually, filamentary discharge mainly occurs between particles or between particles and wall surfaces, while surface discharge mainly exists on the surface of the catalyst. Compared with regularly shaped catalysts, filling materials with a porous structure are more likely to cause surface discharge.¹³

It is observed that the discharge current amplitude of DBD plasma filled with ReS₂ and CsPbBr₃@ReS₂-15 is lower than that of CsPbBr₃, as shown in Fig. 3a. This is consistent with previous works demonstrating that DBD plasma packed with BaTiO₃,⁵ glass beads,⁵ or Ni/Al₂O₃²¹ significantly reduced the current amplitude. Furthermore, CsPbBr₃@ReS₂-15 increases the micro-discharge time, which is the time of the continuous plasma discharge during a discharge period, compared with ReS₂ and CsPbBr₃ (Fig. 3a), implying that a heterogenous photocatalyst improves the plasma discharge characteristics. The uniformity of the plasma discharge for CsPbBr₃@ReS₂-15 is optimal, which is beneficial for plasma-driven CO₂ conversion. In addition, the amounts of the peak-to-peak charge (Q_{pk-pk}) and discharge charge (Q_d) are also one of the indicators of the actual reaction (Fig. S5, ESI[†]). DBD plasma with

CsPbBr₃@ReS₂-15 holds the largest Q_{pk-pk} (545 nC) and Q_d (290 nC) compared with CsPbBr₃ ($Q_{pk-pk} = 500$ nC, $Q_d = 250$ nC) and ReS₂ ($Q_{pk-pk} = 530$ nC, $Q_d = 280$ nC) (Fig. S6, ESI[†]), which indicates that the physical and chemical reactions in the DBD plasma filled with CsPbBr₃@ReS₂-15 are the most violent for CO₂ conversion.

Furthermore, according to the optical absorption spectrum of CsPbBr₃@ReS₂-15 (inset of Fig. S3a, ESI[†]) and optical emission spectrum of DBD plasma filled with CsPbBr₃@ReS₂-15 (Fig. S7, ESI[†]), the photons generated in the plasma can be absorbed by the photocatalyst for CO₂ conversion.²² In fact, the vibrationally excited CO₂ molecules in the plasma can be absorbed on the photocatalyst surface to reduce the potential barrier for the subsequent reduction process, which facilitates the “state-to-state catalytic chemistry” so that high-efficiency photocatalysis is obtained.²³ The spectral bands of various active groups, including CO ($b^3\Sigma_{2u}^- - a^3\Pi_{1g}$), CO₂⁺ ($B^2\Sigma_u^+ - X^2\Pi_g$), and CO₂⁺ ($A^2\Pi_u - X^2\Pi_g$), were detected, as demonstrated in Table S2 and Fig. S7 (ESI[†]).

The vertical ionization energy of CO₂ stands at 13.77 eV,²⁴ while exciting CO₂⁺ from its X²Π_g state to the A²Π_u and B²Σ_u⁺ states necessitates energies of 3.54 eV and 4.31 eV, respectively.²⁵ This indicates that the formation of CO₂⁺ in the X²Π_g, A²Π_u, and B²Σ_u⁺ states within the plasma relies on the presence of high-energy electrons, as outlined in eqn S5–S7 (ESI[†]), while the de-excitation of these active species leads to the emission of photons possessing specific energies, as shown in eqn S8 and S9 (ESI[†]).

The CO yield of the CsPbBr₃@ReS₂-15 photocatalysis, ReS₂ plasma catalysis, and plasma photocatalysis of CsPbBr₃ and CsPbBr₃@ReS₂-15 under the same mass condition was compared. It is observed that the CO yield in the DBD plasma filled with CsPbBr₃@ReS₂-15 ($4.77 \times 10^6 \mu\text{mol g}^{-1} \text{h}^{-1}$) is 56.4% higher than that of ReS₂ ($3.05 \times 10^6 \mu\text{mol g}^{-1} \text{h}^{-1}$), and is much larger than the sole photocatalytic process ($25.67 \mu\text{mol g}^{-1} \text{h}^{-1}$) (Fig. 3d). This highlights the superiority of plasma photocatalysis in the CO₂ conversion. Compared with CsPbBr₃, the ability of the CsPbBr₃@ReS₂-15 heterojunction photocatalyst to absorb light and effectively utilize the photons generated in the DBD plasma is greater, while the presence of a Z-type charge transfer path between ReS₂ and CsPbBr₃ suppresses the recombination of charge carriers, thereby improving the overall CO₂ conversion performance.

In summary, CsPbBr₃ QDs were grown on ReS₂ to construct the CsPbBr₃@ReS₂ heterojunction. The CsPbBr₃@ReS₂ photocatalysts show stronger optical absorption and a type-Z heterojunction, and the photocatalytic CO production is $25.67 \mu\text{mol g}^{-1} \text{h}^{-1}$ for CsPbBr₃@ReS₂-15. The increase in photocatalytic activity is attributed to the improved light absorption and the formation of a Z-scheme heterojunction, facilitating the spatial separation of photogenerated charge carriers. Moreover, DBD plasma filled with CsPbBr₃@ReS₂-15 delivers the optimum CO₂ conversion ratio of 35.60% and energy efficiency of 13.10%. This exceptional performance was obtained due to not only the excellent photocatalytic activity of CsPbBr₃@ReS₂-15, but also the increased micro-discharge time and

satisfactory discharge uniformity of the DBD plasma. This work will promote the development of plasma photocatalytic CO₂ conversion.

This work was supported by the National Natural Science Foundation of China (No. 22072010), and the Natural Science Foundation of Chongqing Municipality (No. CSTB2024NSCQ-LZX0101).

Data availability

The data supporting this article have been included as part of the ESI[†].

Conflicts of interest

There are no conflicts to declare.

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