

Supporting Information

Enhanced CO₂ conversion in dielectric barrier discharge plasma coupling with 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,^{*ab} and Qiang Huang^{*b}

^aState Key Laboratory of Power Transmission Equipment Technology, Chongqing University, Chongqing 400044, China

^bSchool of Optoelectronic Engineering, Chongqing University of Posts and Telecommunications, Chongqing 400065, China

*Corresponding authors

Corresponding author's e-mail address: huangqiang@cqupt.edu.cn (Qiang Huang), qifei@cqupt.edu.cn (Fei Qi), xstang@cqu.edu.cn (Xiaosheng Tang).

Experimental Section

Synthesis of ReS₂

536 mg of NH₄ReO₄ was thoroughly dissolved in 60 ml of deionized water under magnetic stirring. Subsequently, 685 mg of CH₄N₂S was added to the prepared solution and stirred for 30 min. The mixed solution was then transferred to a 100 ml reaction kettle, where a hydrothermal reaction was conducted at 240 °C for 24 h. Finally, after the reaction kettle cooled down, the precipitate was fished out, washed with deionized water, and dried at 60 °C overnight.

Synthesis of CsPbBr₃

CsPbBr₃ was prepared via an anti-solvent method. Initially, 42.55 mg of cesium bromide (CsBr) and 73.4 mg of lead bromide (PbBr₂) were combined in a 10 mL beaker. Subsequently, 0.3 mL of oleylamine, 0.9 mL of oleic acid, and 5 mL of dimethylformamide (DMF) were added to the mixture. The beaker was then placed in a water bath, heated to 60 °C, and stirred for 30 minutes to create the precursor solution. To remove excess ligands from the CsPbBr₃, multiple centrifugal washes with toluene were performed.

Synthesis of CsPbBr₃@ReS₂ heterojunction

The preparation of CsPbBr₃@ReS₂ closely follows the method used for CsPbBr₃. Initially, various masses of ReS₂ are dispersed into corresponding toluene solutions. Subsequently, different volumes of the cesium bromide and lead bromide precursor solutions are taken and added dropwise to the respective ReS₂ toluene solutions under continuous stirring. Afterward, the mixed solution is washed by centrifugation for three times. The precipitate is then collected, dried, and the resulting powder is CsPbBr₃@ReS₂. By adjusting the volume of precursor solution, the volume of toluene, and the mass of ReS₂, the CsPbBr₃@ReS₂ with different molar ratios are obtained, as outlined in Table S1. These samples are designated as CsPbBr₃@ReS₂-10, CsPbBr₃@ReS₂-15, CsPbBr₃@ReS₂-20, and CsPbBr₃@ReS₂-25, respectively.

Sample characterization

The crystal structure of the catalysts was investigated on the X-ray diffraction (XRD) equipment with Cu K α radiation (MADZU, Japan). X-ray photoelectron

spectroscopy (XPS) was used to determine the chemical states and valence bands of the photocatalyst samples on ESCALAB250Xi from Thermo Fisher Scientific. The morphology of the catalysts was determined by scanning electron microscopy (SEM, TESCAN MIRA3). The transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were examined on ZEISS LIBRA 200FE.

Photocatalytic performance test

Photocatalysis experiments were conducted in a sealed glass apparatus, illuminated by a 300 W Xe lamp. The temperature within the apparatus was maintained at 20 °C through a water-cooled circulation system (Labsolar-6A, Beijing Perfect Light Technology Co., Ltd.). For each experiment, 10 mg of the prepared photocatalyst was evenly spread onto a glass substrate measuring $1.1 \times 1.1 \text{ cm}^2$. This substrate was then placed inside the reaction chamber, which had a volume of 100 mL. Subsequently, 20 μL of deionized water was injected into the reaction chamber. Afterward, carbon dioxide (99.99% purity) was introduced into the chamber, establishing a gas pressure of 85-90 kPa. Finally, the components of the mixed gas after photocatalytic reaction were analyzed using a gas chromatograph equipped with FID and TCD detectors (GC, Fuli 9790II).

Plasma catalytic performance test

The experimental setup of the dielectric barrier discharge plasma photocatalysis system is depicted in Figure S8. The DBD plasma reactor consists of a power supply (CTP - 2000, Nanjing Suman Electronics Co., Ltd.), two parallel circular stainless steel electrodes and a quartz tank between the electrodes. The quartz tank consists of a concave plate (external diameter of 9.5 cm, internal diameter of 6 cm, external depth of 1 cm, internal depth of 0.8 cm) and an upper cover (diameter of 9 cm, thickness of 0.2 cm). 10 mg of photocatalyst is introduced into the quartz tank to facilitate the plasma photocatalysis process, while the flow rate of CO_2 is precisely regulated at 50 sccm. The voltage and output current of the DBD reactor are accurately measured using a two-channel oscilloscope, following the protocols outlined in our previous work.[1] Notably, the plasma discharge occurs under normal temperature and pressure

conditions, with the plasma discharge input power maintained at a constant 60 W. Following a reaction duration of 10 minutes, the resulting gas mixture is captured using a reservoir bag for 5 minutes. Subsequently, 100 μL of the gas sample is injected into a gas chromatograph for precise gas product detection. Additionally, 1 μL of the liquid product, which is collected in a cold trap over a period of 3 hours post-reaction, is analyzed using the gas chromatograph for liquid product detection. The optical emission spectroscopic (OES) diagnostics of the DBD plasma were performed with a fiber spectrometer (L/200-1000, ChengDu ArtOptics Instruments Co., Ltd.).

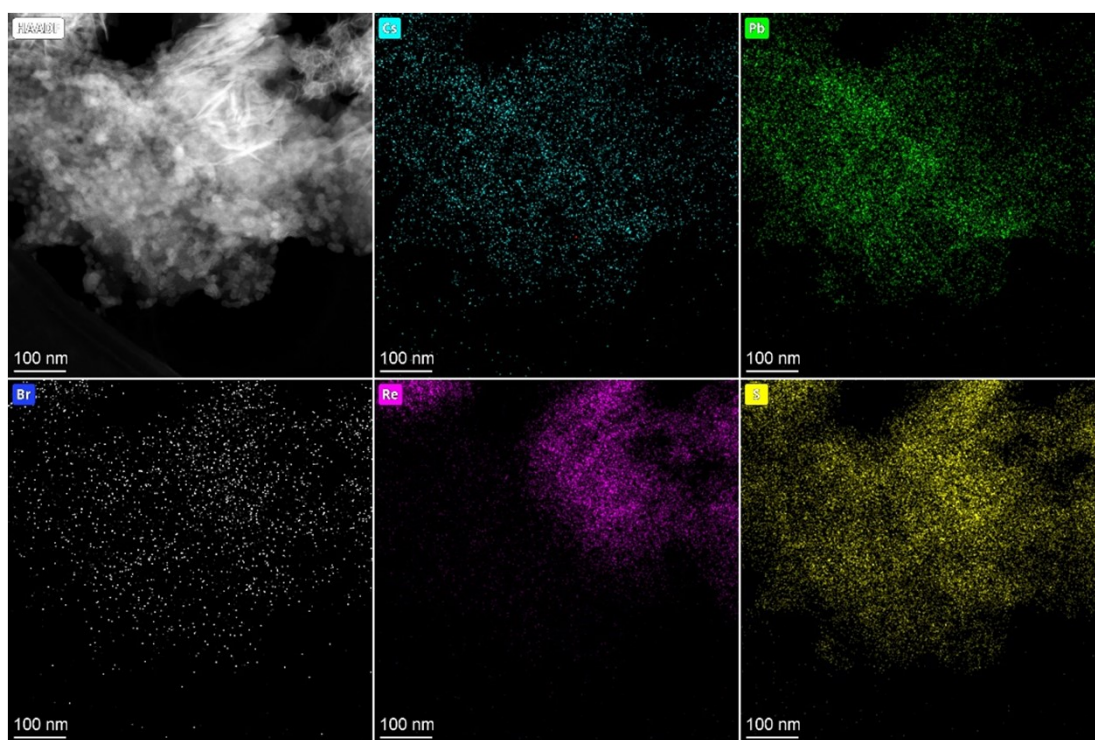


Figure S1 EDS elemental mapping analysis of $\text{CsPbBr}_3@\text{ReS}_2$ -15.

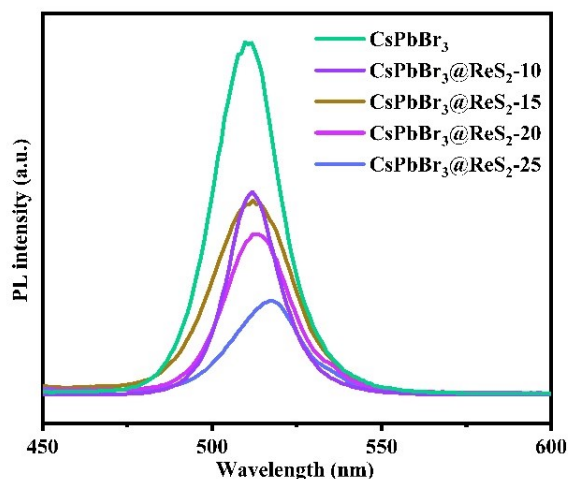


Figure S2 PL spectra of CsPbBr₃ and CsPbBr₃@ReS₂ with different molar ratios under 365 nm motivation.

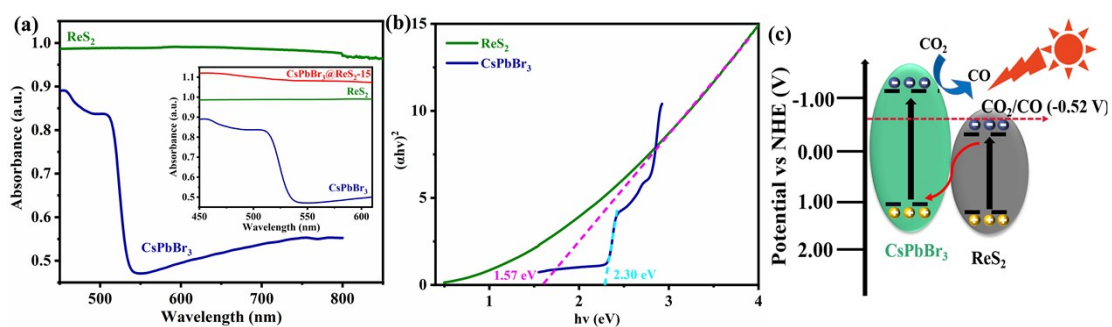


Figure S3 (a) UV-vis of CsPbBr₃, ReS₂ and CsPbBr₃@ReS₂-15, (b) Tauc plots of CsPbBr₃ and ReS₂, (c) band alignment of the CsPbBr₃@ReS₂ heterojunction.

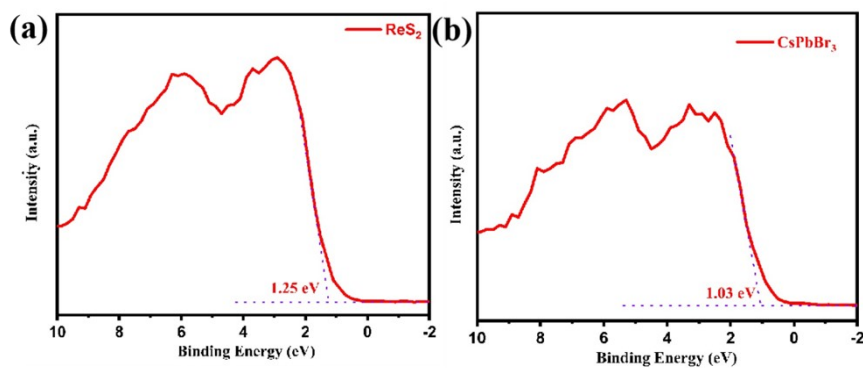


Figure S4 VB XPS spectra of (a) ReS₂ and (b) CsPbBr₃.

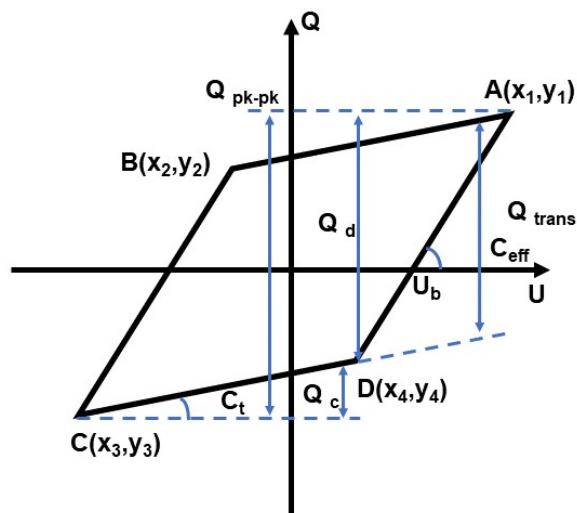


Figure S5 Typical Lissajous figure of the DBD plasma discharge.

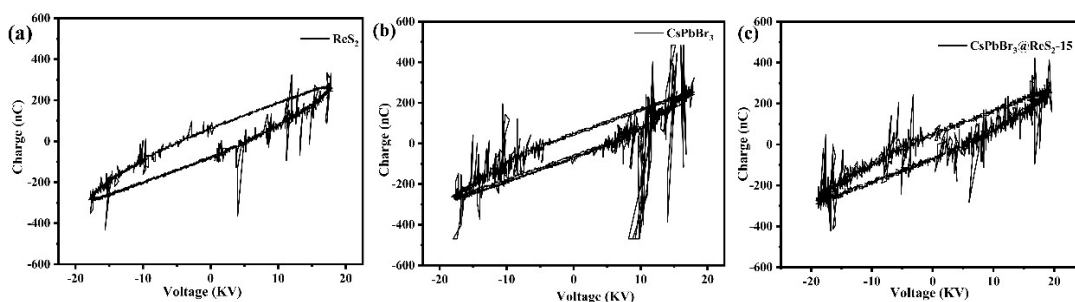


Figure S6 Lissajous figure of (a) ReS_2 , (b) CsPbBr_3 and (c) $\text{CsPbBr}_3@ \text{ReS}_2-15$.

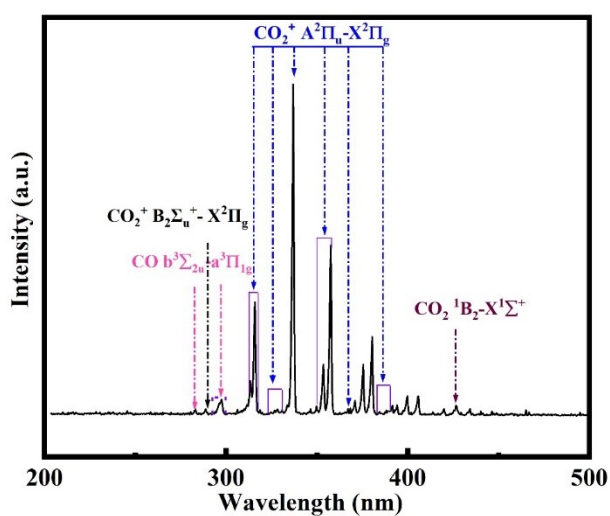


Figure S7 Optical emission spectrum of DBD plasma filled with $\text{CsPbBr}_3@ \text{ReS}_2-15$.

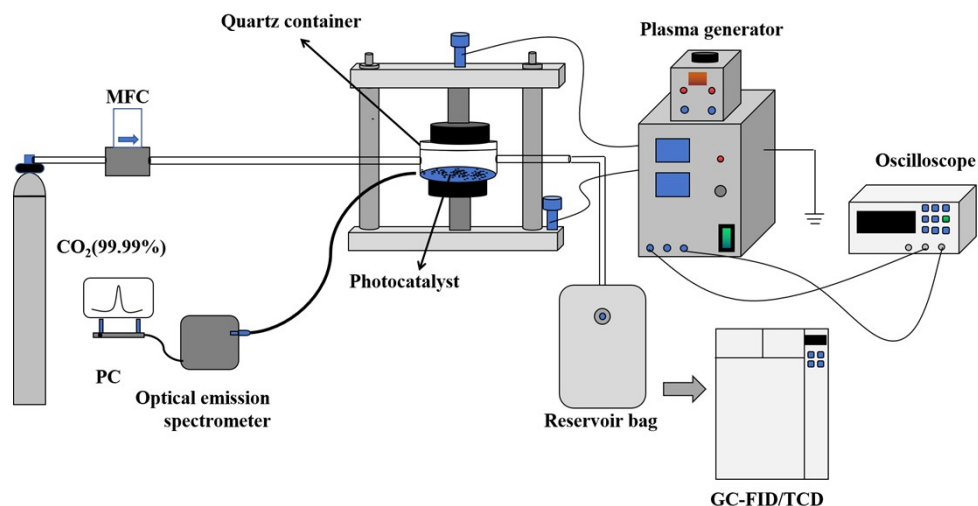


Figure S8 Schematic diagram of the DBD plasma photocatalysis system.

Table S1 The content of raw materials used for the preparation of CsPbBr₃@ReS₂ with different molar ratios

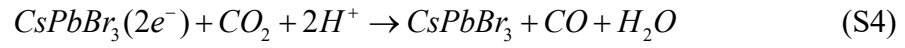
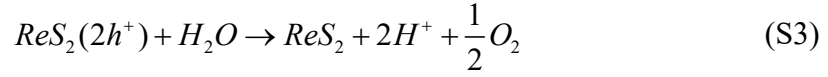
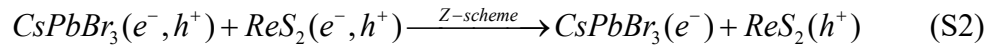
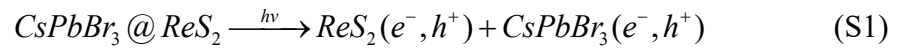
Photocatalyst	Precursor fluid (μL)	Toluene (mL)	ReS ₂ (mg)
CsPbBr ₃ @ReS ₂ -10	487	20.2	40.6
CsPbBr ₃ @ReS ₂ -15	350	14.5	43.3
CsPbBr ₃ @ReS ₂ -20	270	11.2	44.8
CsPbBr ₃ @ReS ₂ -25	220	9.15	46.4

Table S2 The main species detected in the CO₂ plasma via optical emission spectrum.

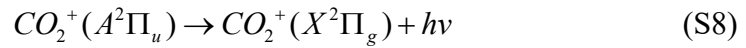
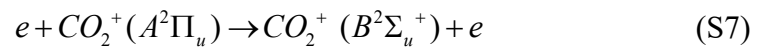
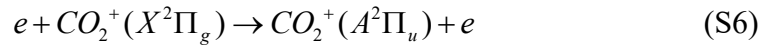
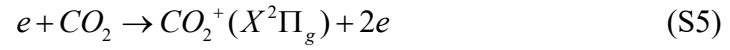
Species	Transition	Wavelength (nm)	Ref.
CO ₂ ⁺	A ² Π _u - X ² Π _g	312.1-317.9	3
		323.1-329.5	2, 3
		336.9-339.4	3
		349.7-357.7	3
		366.4-369.1	3
		383.1-390.1	3
		426.2	6

CO ₂ ⁺	B ² Σ _u ⁺ - X ² Π _g	288.4	4
		289.3	4
CO	b ³ Σ _{2u} ⁻ - a ³ Π _{1g}	283.2	2, 3, 5
		297.1	2
CO ₂	¹ B ₂ -X ¹ Σ ⁺	426	6

Main CO₂ photoreduction processes for CsPbBr₃@ReS₂:



Electrons and photons emission processes in DBD plasma:



References

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