Supporting Information

All-inorganic Perovskite/Graphitic Carbon Nitride Composite for

CO₂ Photoreduction into C1 Compounds under Low Concentrations

of CO₂

Siqi You,^a Shaohong Guo,^a Xue Zhao,^a Min Sun,^a Chunyi Sun,^{*a} Zhongmin Su,^{ab} and Xinlong Wang^{*a}

[a] National & Local United Engineering Laboratory for Power Batteries, Key Laboratory of Polyoxometalate Science of Ministry of Education Department of Chemistry, Northeast Normal University, Changchun, Jilin, 130024 (P.R. China)

[b] Jilin Provincial Science and Technology Innovation Center of Optical Materials and Chemistry, School of Chemistry and Environmental Engineering, Changchun University of Science and Technology Changchun, Jilin, China.

E-mail: suncy009@nenu.edu.cn; wangxl824@nenu.edu.cn; zmsu@nenu.edu.cn

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Experimental Section.

All reagents and solvents for the syntheses were purchased from commercial sources and used as received, unless otherwise indicated.

Materials and methods

Cs-Oleate, CsPbBr3^[1] and g-C3N4^[2], were synthesized according to the literature procedures. SEM images were recorded on XL-30 ESEM-FEG Scanning Electron Microscope. TEM images were recorded on a JEM-2010 transmission electron microscope at an accelerating voltage of 200 kV. XRD patterns were recorded on a Siemens D5005 diffractometer with Cu KR ($\lambda = 1.5418A$) radiation in the range of 10-60°. XPS was performed using an Escalab 250 instrument. UV-Vis absorption spectroscopy was obtained on U-3010 spectrophotometer (Hitachi, Japan). Fluorescence spectra were performed with Eclipse fluorescence spectrophotometer (Varian, USA). Emission lifetime measurements were performed on photon TM 400 technology international master/time quanta master phosphorescence/fluorescence Spectrofluoromete

Synthesis of Cs-Oleate.

 Cs_2CO_3 (0.814 g) and oleic acid (2.5ml) were loaded in a 100ml flask with 1octadecene (10ml), the mixture was heated to 120 °C in vacuum for one hour. Then, heated to 150 °C under Ar flow and magnetic stirring, until cesium carbonate and oleic acid were completely reacted. After that, the solution was cooled to room temperature under N₂, Cs-Oleate needs to be heated before the synthesis of CsPbBr₃.

Synthesis of CsPbBr₃

PbBr₂ (367.01 mg) was put into a 50 ml beaker with DMF (20 ml), hexanoic acid (232.32 mg) and octylamine (258.48 mg). Until PbBr₂ was absolutely dissolved. Csoleate solution (prepared in the above experimental part) was added to reaction liquid. Finally, 0.5 ml of mixed solution was added to one beaker, followed 20 ml of toluene was added to this beaker. Liquid was centrifuged (8000r/min, 5min), the solid was added to ethyl acetate for washing and centrifuged again. After washing for 2-3 times, CsPbBr₃ solid was dried at room temperature.

Synthesis of g-C₃N₄

Under the condition of air, Urea (10 g) was placed in a crucible and heated to 550 degrees centigrade at a speed of 0.5° C/min. The reaction lasted for 2.5 hours. After the reaction, it was cooled at room temperature.

Synthesis of CsPbBr₃@g-C₃N₄

The g-C₃N₄ (30mg) were added into toluene (5 ml), respectively. The solution was ultrasonicated for 2 hours. Subsequently, 1mg CsPbBr₃ was mixed with the g-C₃N₄ solution under magnetic stirring for 6 hours with silver paper cover. Finally, the CsPbBr₃@g-C₃N₄ composites were obtained after centrifuging (8000r/min, 5min) and washing (by ethyl acetate) three times followed by drying at room temperature. The results show that 1.61wt% (based on Pb) amount of CsPbBr₃ was loaded and the corresponding sample is denoted as CsPbBr₃@g-C₃N₄.

Photocatalytic CO₂ reduction tests

The CO₂ reduction test was carried through in a 50 ml sealed quartz tube with ethyl acetate (6ml) and catalyst (5mg). The temperature of the reaction solution was maintained at 20 °C controlled by a flow of water during the reaction. Then, the system was irradiated with a 300 W Xe lamp with a AM 1.5 cutoff filter under stirring. The produced gases (CO and CH_4) were detected using a gas chromatography

Photocurrent Measurements

Our sample, Ag/AgCl electrode and Pt-wire electrode were employed as the working, reference and counter electrode, respectively. Irradiation was carried out by using a 300 W xenon lamp with a AM 1.5 filter. The tetrabutylammonium hexafluorophosphate solution (0.1M) was used as the electrolyte. The working electrodes were prepared by spreading aqueous slurries of various samples on FTO glass substrate, using adhesive tapes as spaces to obtain a 1 cm \times 1 cm electrode.



Figure S1. XP spectrum of g- C_3N_4 (a) C element (b) and N element (c) in bare g- C_3N_4 .



Figure S2. XP spectrum of CsPbBr₃ (a), its element Cs (b), Pb (c) and Br (d).



Figure S3. Kubelka-Munk transformed reflectance spectra of CsPbBr₃.



Figure S4. VB -XPS spectra of CsPbBr₃

Table 1. Lifetimes of CsPbBr₃, CsPbBr₃@g-C₃N₄, g-C₃N₄.

Sample	$\tau_{\rm l}/{\rm ns}$ (%)	$ au_2$ / ns (%)	τ_{3} / ns (%)	$\tau_{average}/ns$
CsPbBr ₃	58.81 (44.76)	393.37 (55.24)	/	243.62
$CsPbBr_3@g-C_3N_4$	4.70 (59.89)	39.33 (40.11)	/	18.59
g-C ₃ N ₄	2.37 (67.26)	9.06 (23.59)	42.78 (9.15)	7.65



Figure S5. X-ray diffraction pattern (XRD) for the as-prepare $CsPbBr_3@g-C_3N_4$ before and after reaction.



Figure S6. GC-MS results of ${}^{13}CH_4$ produced over CsPbBr₃@g-C₃N₄ from ${}^{13}CO_2$ isotope experiment in ethyl acetate.

Photocatalyst	photosensitizer	Products	μ mol g ⁻¹ h ⁻¹	Light source	CO ₂ vol%	Ref
CsPbBr ₃ @g-C ₃ N ₄	/	CH ₄	7.08	300 W Xe	11%	This work
CsPbBr ₃ @g-C ₃ N ₄	/	СО	1.67	300 W Xe	11%	This work
C_3N_4	/	СО	2.6	100 W Xe	20%	3
OT-C ₃ N ₄	/	СО	2.34	100 W Xe	20%	3
OR-C ₃ N ₄	/	СО	0.7	100 W Xe	20%	3
TNT	/	CH ₄	3.7	100 W Xe	1%	4
C,N-TNT01	/	CH ₄	6.25	100 W Xe	1%	4
C,N-TNT03	/	CH ₄	4.6	100 W Xe	1%	4
C,N-TNT06	/	CH_4	9.75	100 W Xe	1%	4
C,N-TNT-1	/	CH_4	6.75	100 W Xe	1%	4

Table 2. The work of reported papers for diluted CO_2 photoreduction. without noble metal.

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