

Supplemental Material

To

**Fabricating a type II heterojunction by growing lead-free  
perovskite Cs<sub>2</sub>AgBiBr<sub>6</sub> in situ on graphite-like g-C<sub>3</sub>N<sub>4</sub> nanosheets  
for enhanced photocatalytic CO<sub>2</sub> reduction**

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## ***Experimental Sections***

**Materials:** Cesium Bromide (CsBr, 99.5%, AR grade), Silver bromide (AgBr, 99.9%, AR grade) and Bismuth (III) bromide (BiBr<sub>3</sub>, ≥98%, AR grade) were achieved from Shanghai Macklin Biochemical Co., Ltd (Shanghai, China). Dicyandiamide (≥99%, AR grade) was obtained from Shanghai Meryer Chemical Technology Co., Ltd (Shanghai, China). N, N-dimethylformamide (DMF, ≥99.5%, AR grade) and Dimethyl sulfoxide (DMSO, 98%, AR grade) were gained from Tianjin Fuyu Fine Chemical Co., Ltd. (Tianjin, China). All the above chemicals were commercially available and used without further purification.

**Synthesis of g-C<sub>3</sub>N<sub>4</sub> nanosheets:** Synthesis of g-C<sub>3</sub>N<sub>4</sub> nanosheets is similar to the previous reports.<sup>1</sup> Firstly, 2g dicyandiamide was dispersed in 50 mL DI water, and a homogeneous solution were obtained after ultrasonic treatment for 30 min. Then, the acquired solution was transferred into a 150 mL Teflon-lined stainless-steel autoclave. The autoclave then put into an oven and the temperature were setting at 200 °C for 4 hours. After natural cooling of autoclave, residuals were centrifuged and collected, followed by completely dry treatment. The dried white powder then putted into a muffle furnace, the temperature of muffle furnace was set at 550 °C and the heating time were setting for 2 hours. After above process, the g-C<sub>3</sub>N<sub>4</sub> nanosheets were obtained.

**Preparation of g-C<sub>3</sub>N<sub>4</sub>@Cs<sub>2</sub>AgBiBr<sub>6</sub> nanocomposites:** In-situ crystallization method<sup>2</sup> was used to prepare g-C<sub>3</sub>N<sub>4</sub>@Cs<sub>2</sub>AgBiBr<sub>6</sub> (CABB) composite photocatalysts. First, 25 mg g-C<sub>3</sub>N<sub>4</sub> nanosheets were dispersed in 1 mL DMF under ultrasonic treatment

(30 min), resulting in a uniform solution. The CABB precursor solution was prepared by dissolving CsBr, AgBr, and BiBr<sub>3</sub> (molar ratio=2: 1: 1) in a mixture of DMF and DMSO (total volume = 1mL). Next, the CABB precursor solution was transferred into the g-C<sub>3</sub>N<sub>4</sub> nanosheet suspensions and subjected to ultrasonic treatment for 30 min. Next, the mixed precursor containing g-C<sub>3</sub>N<sub>4</sub> and CABB were added dropwise to a 25 mL toluene solution with vigorous stirring. After 5 min of stirring, the product was centrifuged and put in a vacuum dryer for 6 hours at 120 °C. g-C<sub>3</sub>N<sub>4</sub>@CABB nanocomposites with different CABB content were prepared by maintaining the following concentrations of CsBr in CABB: 0.014, 0.028, 0.056, and 0.112 mmol (CsBr: AgBr: BiBr<sub>3</sub> with mole ratio=2:1:1). The synthesized nanocomposites were labeled as g-C<sub>3</sub>N<sub>4</sub>@CABB<sub>1</sub>, g-C<sub>3</sub>N<sub>4</sub>@CABB<sub>2</sub>, g-C<sub>3</sub>N<sub>4</sub>@CABB<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub>@CABB<sub>4</sub> respectively.

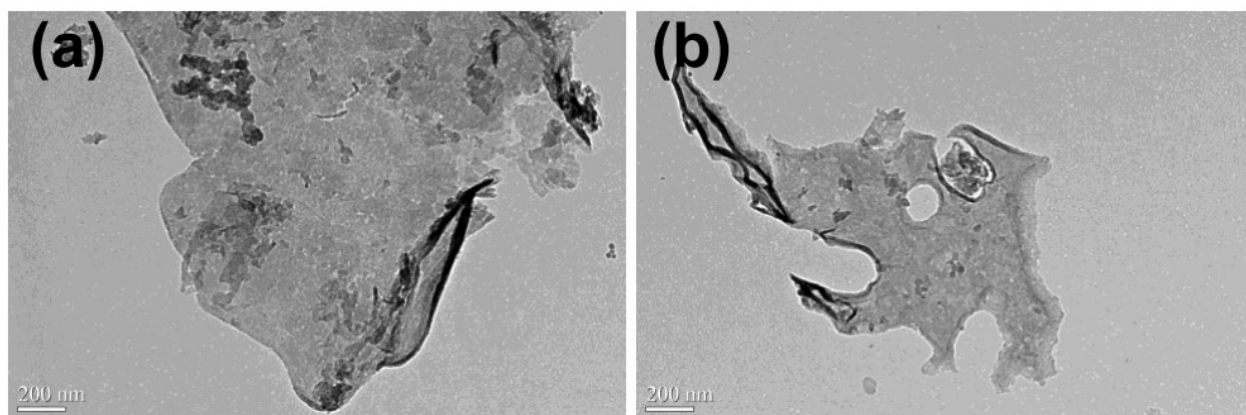
**Characterizations:** X-ray diffraction (XRD) patterns were obtained using a Bruker AXS D8 Discover X-ray diffractometer at a wavelength of Cu K (1.79) to characterize the material's crystal structure. X-ray photoelectron spectroscopy (XPS) measurements for elemental composition was processed on the air-exposed composites film surface and composites powder by an AXIS ULTRA (England, KRATOS ANALYTICAL Ltd.) using an Al mono K $\alpha$  X-ray source (1486.6 eV) operated at 150 W. SEM images were acquired on a JEOL 7800F Field Emission Scanning Electron Microscope, with an EDS mapping system for elemental x-ray analysis. Ultraviolet and visible absorption (UV-vis) spectra were collected using a Cary 5000 UV-Vis-NIR spectrophotometer. A FEI G2F30 electron microscope

operated at 200 kV with a Gatan SC 200 CCD camera equipped with an EDS was used for transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) and to determine the elemental composition. The steady-state photoluminescence spectra (PL) were collected using a F4600 Fluorescence spectrophotometer (Hitachi) under excitation at 405 nm. The time-resolved fluorescence measurements were detected with a FLS-1000 steady state and transient state fluorescence spectrometer (Edinburgh Instruments Ltd.).

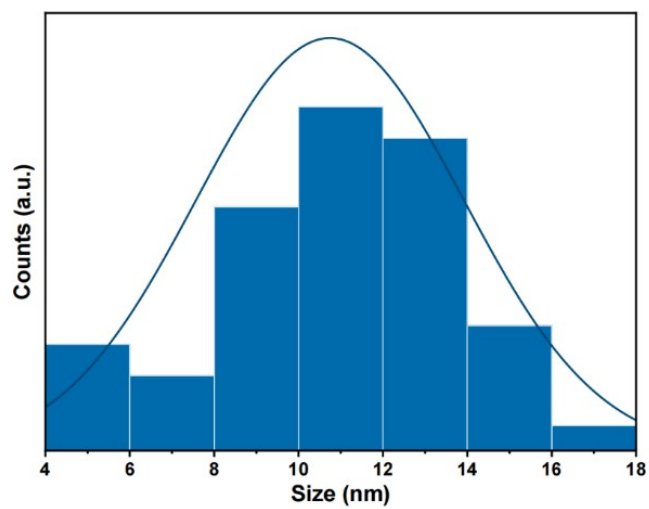
**Photocatalytic Experiments:** Measurement on photoreduction CO<sub>2</sub> under visible-light illumination ( $\lambda > 420$  nm, 80 mW cm<sup>-2</sup>) of g-C<sub>3</sub>N<sub>4</sub>, CABB and g-C<sub>3</sub>N<sub>4</sub>@CABB<sub>3</sub> were carried out in the solution of 99 mL ethyl acetate and 1 ml water, with 10% volume triethylamine as the sacrificial agent.<sup>3</sup> magnetic stirring and ultrasonication was used to disperse the pellet suspension. The suspension then transferred to a quartz glass reactor with a condensing water circulation system, and Ar gas was introduced at a flow rate of 20 sccm for 10 min to fully replace the air, followed by high purity CO<sub>2</sub> gas (5N) at a flow rate of 8 sccm. The light source was a 300 W xenon lamp with a 420 nm cutoff filter. The light intensity was 80 mW/cm<sup>2</sup> and the incident area was  $\pi*(4.5/2)^2$  cm<sup>2</sup>. To ensure full reaction, the reaction was carried out under magnetic stirring at 500 rpm/min. Reaction products were analysis by Agilent GC7890 (FID & TCD).

**Electrochemical measurements:** electrochemical impedance spectroscopy (EIS) tests were carried out on an electrochemical workstation (CHENHUA760, China). A three-electrode configuration cell was used with the assembled photoelectrodes (g-C<sub>3</sub>N<sub>4</sub>,

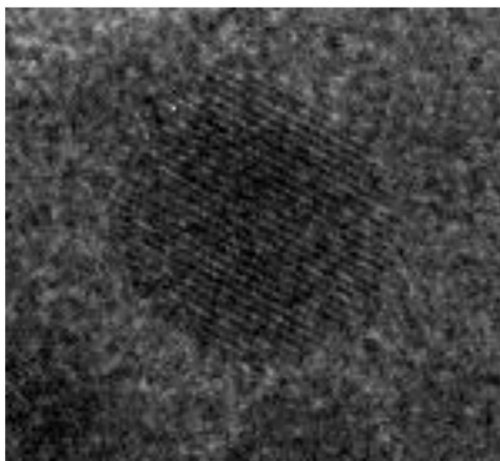
CABB and  $g\text{-C}_3\text{N}_4@\text{CABB}_3$  composite samples on FTO glass) as the working electrode, the Pt mesh as counter electrode, and the Ag/AgCl (in 3 M KCl) as the reference electrode.



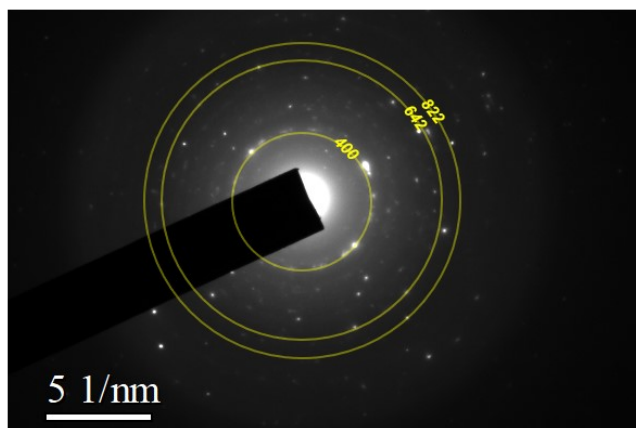
**Figure S1.** TEM image of  $g\text{-C}_3\text{N}_4$  nanosheets.



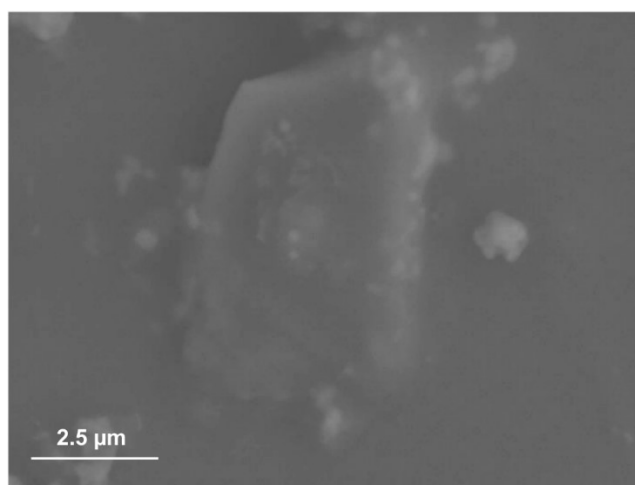
**Figure S2.** Size distribution of CABB in  $g\text{-C}_3\text{N}_4@\text{CABB}_3$ .



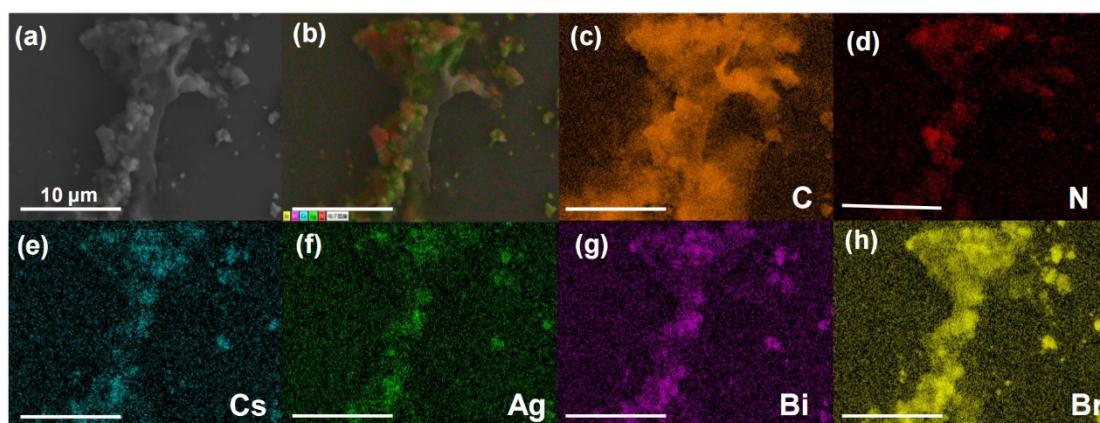
**Figure S3.** HR-TEM image of CABB loaded on g-C<sub>3</sub>N<sub>4</sub>



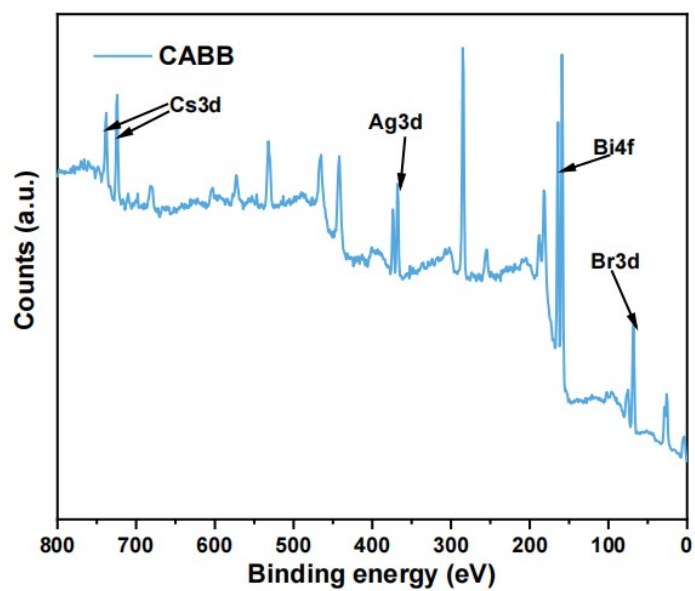
**Figure S4.** Diffraction pattern of g-C<sub>3</sub>N<sub>4</sub>@CABB<sub>3</sub>.



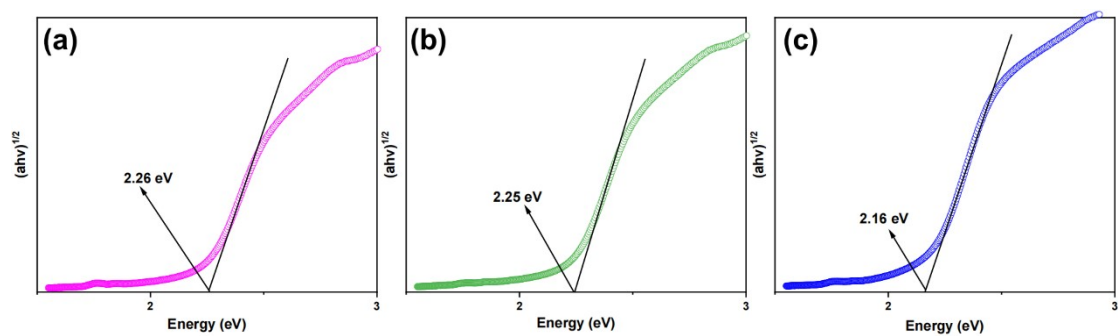
**Figure S5.** SEM image of g-C<sub>3</sub>N<sub>4</sub>@CABB<sub>3</sub>.



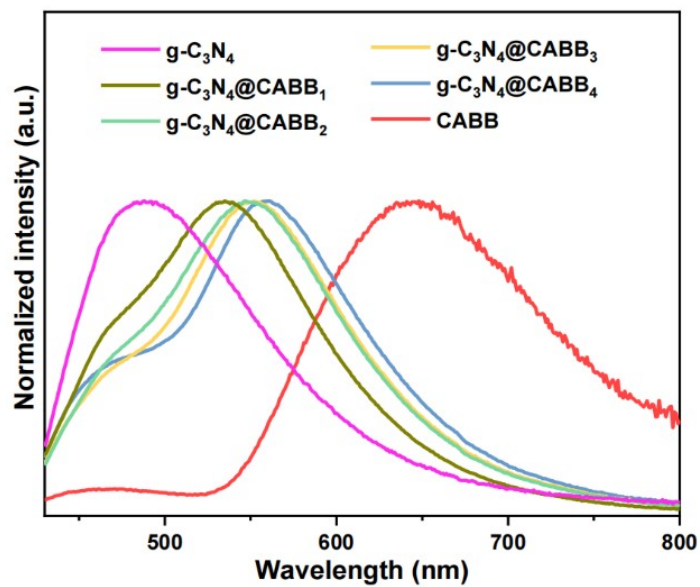
**Figure S6.** SEM and element mapping image of  $g\text{-C}_3\text{N}_4@\text{CABB}_3$ .



**Figure S7.** XPS spectra CABB.

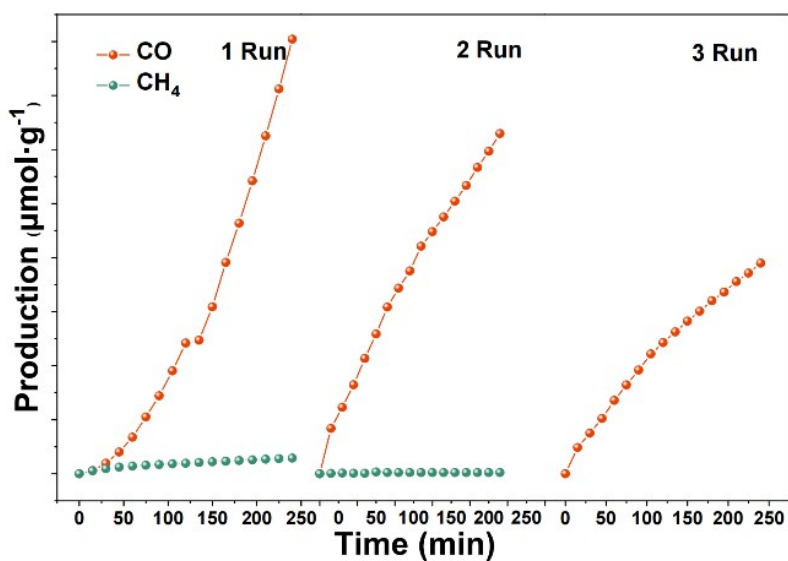


**Figure S8.** Tauc plot of  $g-C_3N_4@CABB_1$  (a),  $g-C_3N_4@CABB_2$  (b) and  $g-C_3N_4@CABB_4$  (c).

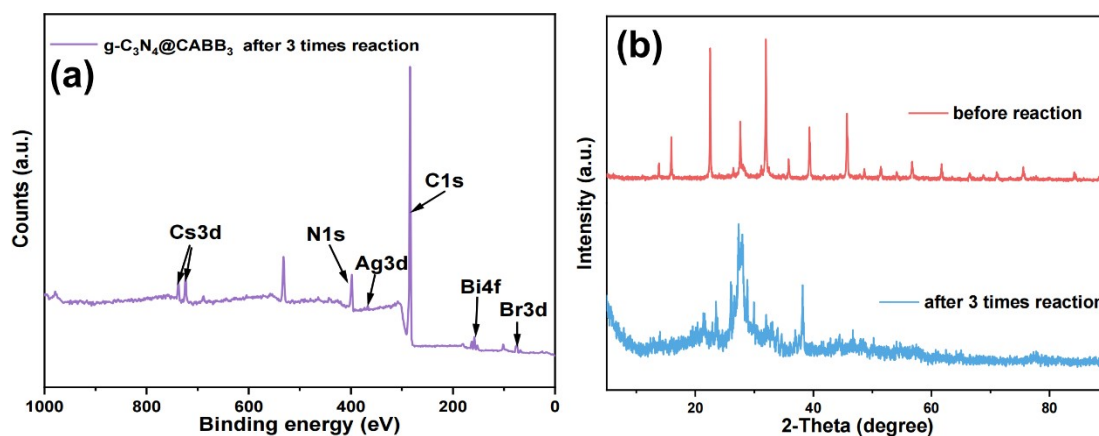


**Figure S9.** normalized PL spectra of  $g-C_3N_4$ , CABB and  $g-C_3N_4@CABB_X$  ( $X=1, 2, 3$  and 4).





**Figure S10.** Recycling runs of  $g\text{-C}_3\text{N}_4@\text{CABB}_3$  towards  $\text{CO}_2$  reduction.



**Figure S11.** (a) XPS spectra of  $g\text{-C}_3\text{N}_4@\text{CABB}_3$  after 3 times utilization. (b) XRD pattern of  $g\text{-C}_3\text{N}_4@\text{CABB}_3$  after 3 times utilization.

## REFERENCES

1. M. Ou, W. Tu, S. Yin, W. Xing, S. Wu, H. Wang, S. Wan, Q. Zhong and R. Xu, *Angewandte Chemie International Edition*, 2018, **57**, 13570-13574.
2. H.H. Zhang, Z.C. Zhou, Y.J. Dong, L. Zhang, H.Y. Chen and D.B. Kuang, *Solar RRL*, 2021, **5**, 2100559.
3. Y. Wang, H. Huang, Z. Zhang, C. Wang, Y. Yang, Q. Li and D. Xu, *Applied Catalysis B: Environmental*, 2021, **282**, 119570.
4. A. Pan, X. Ma, S. Huang, Y. Wu, M. Jia, Y. Shi, Y. Liu, P. Wangyang, L. He and Y. Liu, *The Journal of Physical Chemistry Letters*, 2019, **10**, 6590-6597.
5. T. Zhao, D. Li, Y. Zhang and G. Chen, *Journal of Colloid and Interface Science*, 2022, **628**, 966-974.
6. R. Cheng, H. Jin, M. B. J. Roeffaers, J. Hofkens and E. Debroye, *ACS Omega*, 2020, **5**, 24495-24503.
7. S. You, S. Guo, X. Zhao, M. Sun, C. Sun, Z. Su and X. Wang, *Dalton Transactions*, 2019, **48**, 14115-14121.