

Incorporation of Cesium Lead Halide Perovskites into g-C₃N₄ for Photocatalytic CO₂ Reduction

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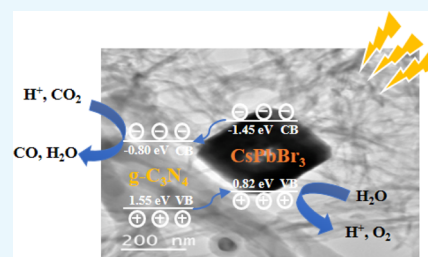


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Supporting Information

ABSTRACT: CsPbBr₃ perovskite-based composites so far have been synthesized by postdeposition of CsPbBr₃ on a parent material. However, *in situ* construction offers enhanced surface contact, better activity, and improved stability. Instead of applying a typical thermal condensation at highly elevated temperatures, we report for the first time CsPb(Br_xCl_{1-x})₃/graphitic-C₃N₄ (CsPbX₃/g-C₃N₄) composites synthesized by a simple and mild solvothermal route, with enhanced efficacy in visible-light-driven photocatalytic CO₂ reduction. The composite exhibited a CO production rate of 28.5 μmol g⁻¹ h⁻¹ at an optimized loading amount of g-C₃N₄. This rate is about five times those of pure g-C₃N₄ and CsPbBr₃. This work reports a new *in situ* approach for constructing perovskite-based heterostructure photocatalysts with enhanced light-harvesting ability and improved solar energy conversion efficiency.



1. INTRODUCTION

The increasing emission of greenhouse carbon dioxide (CO₂) and the imminent shortage of energy supplies have drawn extensive public attention. Thanks to the pioneering work on TiO₂ in water splitting,¹ artificial photosynthesis has become one of the most promising methods to convert solar energy to chemical resources such as CO, CH₄, and CH₃OH.² It is generally known that CO₂ is a stable linear molecule and its unreactive nature requires very high energy or strong reductive agents to initiate its reduction reaction. Moreover, the single-electron reduction of CO₂ to the anion radical CO₂^{•-} has a strong negative electrochemical potential of -1.9 V *versus* the normal hydrogen electrode (NHE).³ To circumvent this problem, Tran *et al.* reported that proton-assisted transfer of multiple electrons enables straightforward CO₂ photoreduction.⁴ So far, a substantial number of materials and their composites have been reported to function as electrocatalysts and/or photocatalysts for CO₂ reduction.⁵ However, the search for new photocatalytic materials with improved performance is still ongoing.

Recently, halide perovskites with an ABX₃ structure [A = CH₃NH₃⁺ (MA), HC(NH₂)₂⁺ (FA), Cs⁺; B = Pb²⁺, and Sn²⁺; X = I⁻, Br⁻, and Cl⁻] have emerged as an excellent class of light absorbers for the use in solar cells.⁶ These materials have attracted attention around the globe for their excellent properties: cheap and easy fabrication process, tunable small band gaps, high absorption coefficients, and extremely long-range balanced electron and hole transport lengths.^{6,7} What is more, owing to the energy level of the conduction band (CB), they have a good reduction ability to achieve H₂ generation and CO₂ reduction.⁸ However, halide perovskites are not stable in a polar environment, and reactions are conventionally performed in nonpolar or relatively low polarity solvents.

Fortunately, all-inorganic perovskites, especially cesium lead halide (CsPbX₃, X = Cl, Br, and I), offer an improved stability and nonhygroscopicity.^{9,10} As a prominent representative, cesium lead bromide (CsPbBr₃) has been seen as a potential candidate for photocatalysis, especially for photocatalytic CO₂ reduction.^{11–14}

Several strategies have been employed to further improve the activity and stability of halide perovskites in polar solvents. First, CsPbX₃ is coupled with other photocatalysts, including TiO₂,¹⁵ g-C₃N₄,¹⁶ MXene,¹⁷ and UiO-66-NH₂.¹⁸ Secondly, it can be encapsulated in porous materials such as metal–organic frameworks (MOFs, ZIF-8,¹⁹ and ZIF-67²⁰) or core–shell structure, which helps in maintaining its structural stability and photoactivity. Solar cell-like architectures have been explored to prevent direct contact of perovskites with polar solvents, providing another effective route toward long-term stabilization.^{21,22} The anion exchange approach is also widely investigated to tune the optical and structural properties of CsPbX₃.^{23–25}

Herein, we construct a novel CsPbX₃/g-C₃N₄ composite by *in situ* polymerization for the first time. Graphitic carbon nitride (g-C₃N₄) with a graphene-like two-dimensional structure, high physicochemical stability, and a medium band gap (2.7 eV) has been introduced as a promising candidate for visible light photocatalytic conversion of CO₂ and is widely

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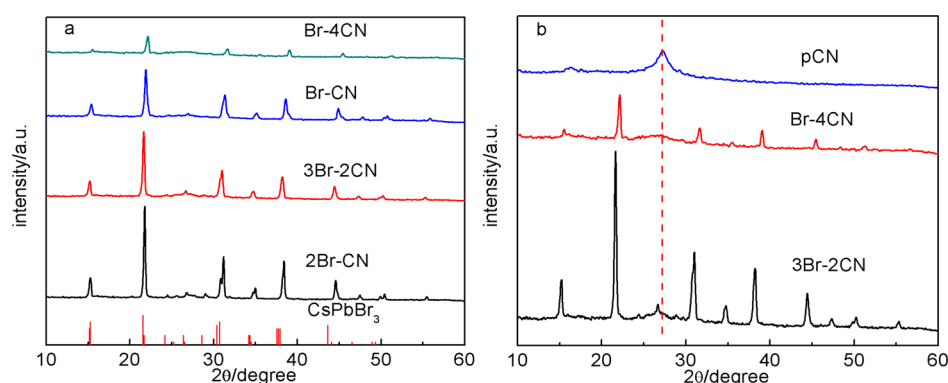


Figure 1. XRD patterns of (a) all the synthesized $\text{CsPbX}_3/\text{g-C}_3\text{N}_4$ composites and (b) pCN, 3Br-2CN and Br-4CN.

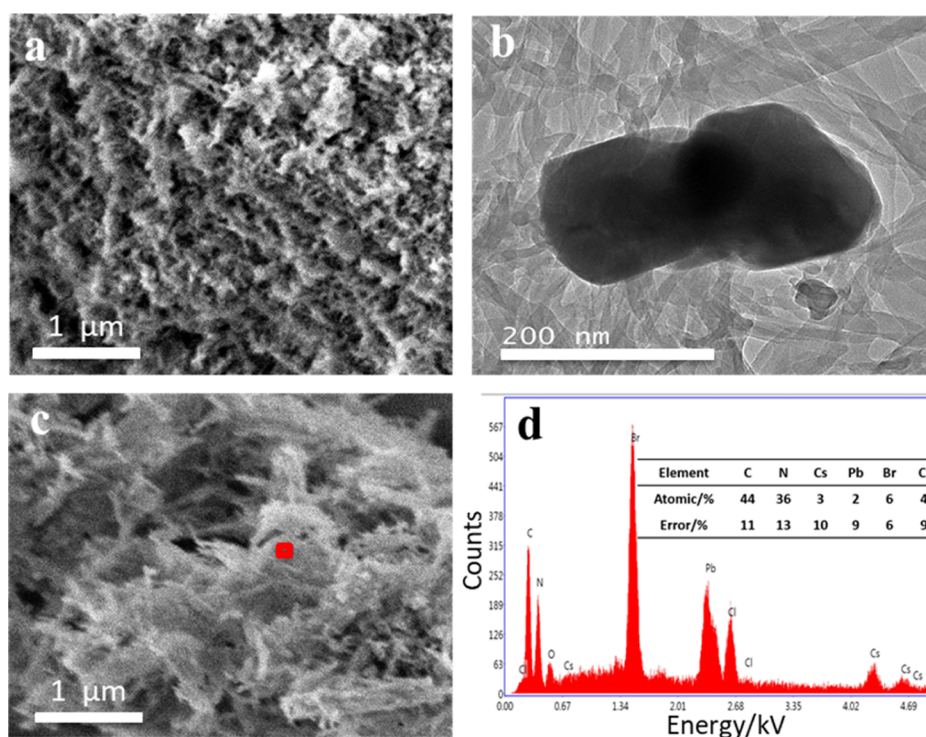


Figure 2. (a) Typical SEM image of pCN, (b) TEM, and (c) SEM images of 3Br-2CN; (d) EDS result of the selected region in (c).

used to hybridize with other photocatalysts.^{26–28} Compared to the postsynthesis self-assembly of the composite,²⁷ *in situ* construction could offer enhanced surface contact, better activity, and improved stability.²⁹ Different from the typical thermal condensation at 550 °C to synthesize $\text{g-C}_3\text{N}_4$, solution synthesis is a mild route suitable for *in situ* perovskite-based composite construction.³⁰ In this approach, acetonitrile is used as the solvent instead of water or other polar solvents, to minimize perovskite degradation.

2. RESULTS AND DISCUSSION

A series of $\text{CsPbX}_3/\text{g-C}_3\text{N}_4$ composites with varying composition have been synthesized by *in situ* growth, as described in the [Experimental Section](#). X-ray diffraction (XRD) measurements were performed to reveal the crystal structure of the parent components (CsPbBr_3 and $\text{g-C}_3\text{N}_4$) and all composites. Starting with orthorhombic CsPbBr_3 (Figure S1a), the composites maintain the original perovskite crystal structure. With increasing amounts of $\text{g-C}_3\text{N}_4$ introduced into the system, the peaks corresponding to the (100), (110),

(111), (200), (211), and (202) diffractions of CsPbBr_3 monotonically shift toward higher angles because of the lattice contraction caused by Br-to-Cl anion exchange during the synthesis.³¹ Simultaneously, the (002) peak of $\text{g-C}_3\text{N}_4$ at 27.4° becomes dominant, while the diffraction peaks of CsPbBr_3 get weaker (Figure 1b).

The morphology and elemental composition of the as-synthesized samples were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). pCN is composed of a network of nanobelts (Figure 2a), and pure CsPbBr_3 has a uniform cubic shape (Figure S2). In the further discussion on characterization, especially the 3Br-2CN composite is focused on because it exhibited the best photocatalytic performance, as will be discussed at the end of this section. 3Br-2CN mainly exhibits the same morphology as pCN (Figures 2b and S2a); nevertheless, energy-dispersive spectrometry (EDS) elemental analysis of a selected region confirms the coexistence of both CsPbX_3 and $\text{g-C}_3\text{N}_4$ (Figure 2c). Moreover, TEM imaging and element

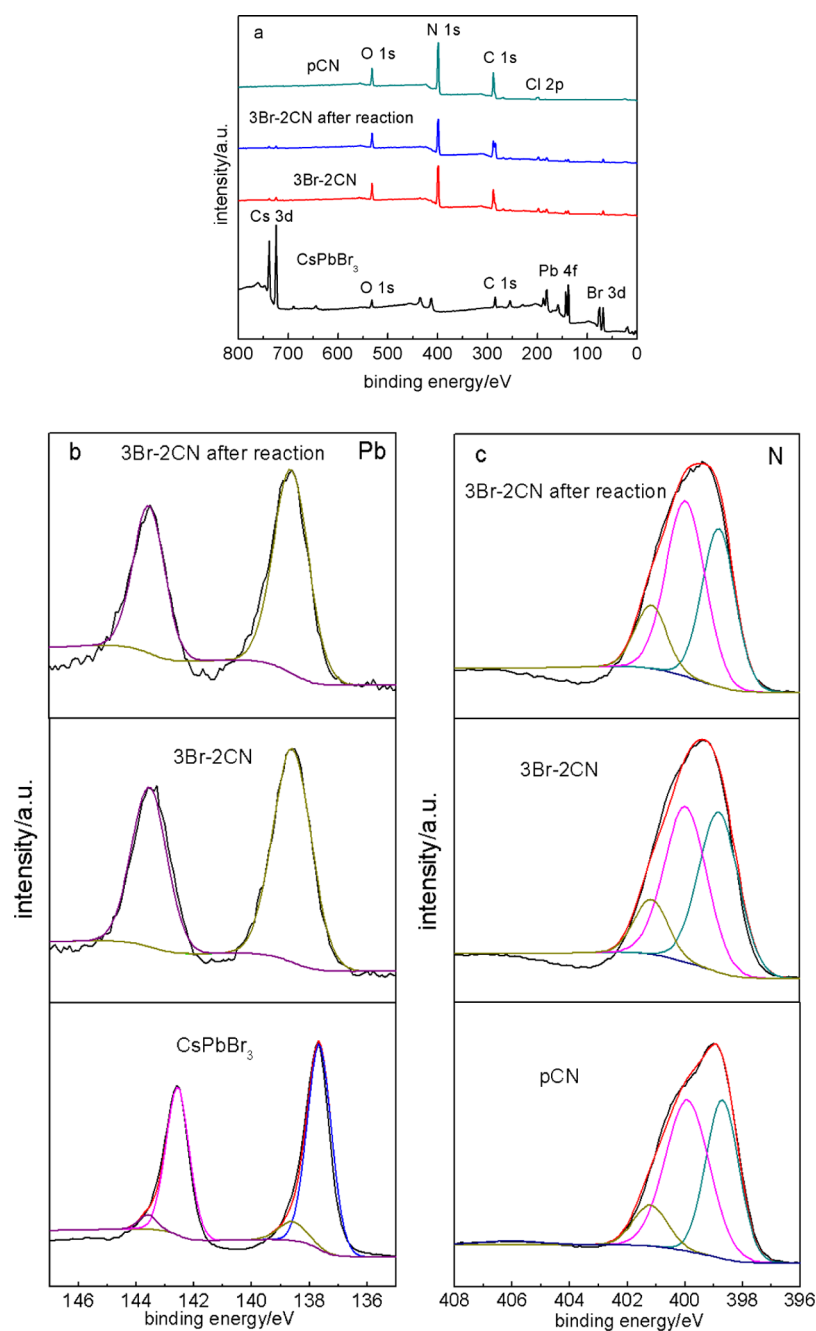


Figure 3. XPS spectra of CsPbBr₃ and 3Br-2CN (a) survey, (b) Pb 4f, and (c) N 1s.

mapping of 3Br-2CN (Figures 2b and S3) support the *in situ* growth of g-C₃N₄ on CsPbBr₃, encapsulating the perovskite.

Thermal stability and sample composition were investigated by thermogravimetric analysis (TGA) (Figure S4). pCN has two weight loss regions: the first one is when heating from room temperature to 100 °C, which is due to the adsorbed H₂O; the second one is from 350 to 500 °C. Above 500 °C, pCN is fully decomposed, and hardly any substance remains.³² Pure CsPbBr₃ (onset *ca.* 600 °C) is more thermally stable than pure g-C₃N₄.³³ Hence, the rapid weight decrease of the composites in the temperature range of 350–550 °C could be assigned to the decomposition of g-C₃N₄. Notably, the composites possess higher decomposition temperatures than that of pCN, which reveals the higher thermal stability of the composites.

The surface chemical composition and chemical states of the as-synthesized composites were revealed by an X-ray photoelectron spectroscopy (XPS) survey spectrum and relative high-resolution spectra. 3Br-2CN shows distinct signals belonging to C, N, O, Cl, Cs, Pb, and Br, suggesting the successful synthesis of the CsPbX₃/g-C₃N₄ composite (Figure 3a). Notably, the composite demonstrates a decreased intensity of Cs 3d, Pb 4f, and Br 3d peaks compared to the pure CsPbBr₃, suggesting that the CsPbBr₃ particles were encapsulated by g-C₃N₄.^{34,34}

Four distinct chemical states of carbon are identified (Figure S5b). Typically, the peak centered at 284.8 eV comes from sp² C–C bonds, while the peaks at 286.3 and 288.6 eV are ascribed to C–N bonds in carbon species and sp² bonded carbon (N=C=N) in the triazine rings, respectively.³⁵ The peak at 290 eV

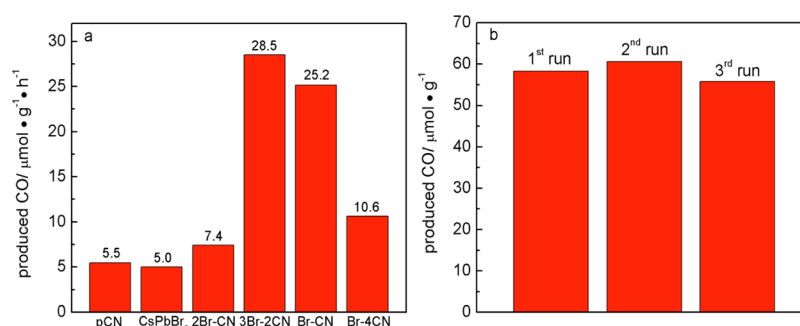


Figure 4. Photocatalytic CO₂ reduction on (a) pCN, CsPbBr₃, and CsPbX₃/g-C₃N₄ composites under visible light irradiation $\lambda > 420$ nm; (b) stability test of CO₂ photoreduction on 3Br-2CN for three consecutive runs of 2 h each.

Table 1. Physical Parameters of the Prepared CsPbX₃/g-C₃N₄ Catalysts

sample	pCN	CsPbBr ₃	2Br-CN	3Br-2CN	Br-CN	Br-4CN
$S_{\text{BET}}/\text{m}^2 \text{g}^{-1}$	45	0.2	21	68	54	47
bandgap/eV	2.35	2.27	2.42	2.46	2.47	2.38

is ascribed to deposited carbon. As can be seen in Figure 3c, in the N 1s spectra of pCN can be fitted according to traditional g-C₃N₄.³⁶ The dominating peak at 398.6 eV is from the sp² nitrogen (C=N-C). The peak belonging to the tertiary nitrogen bonded to carbon atoms in the form of N-(C)3 is at 399.9 eV and the one at 401.2 eV originates from amino functional groups (C-N-H). The same patterns of C 1s and N 1s spectra can be found in 3Br-2CN, confirming the successful formation of the composite.

Cs 3d peaks observed in the range of 720–745 eV shift to higher binding energy in the composite (Figure S5a). This phenomenon has also been found in other CsPbBr₃ composites.³⁷ The Pb 4f spectra (Figure 3b) of pure CsPbBr₃ show two main peaks of metallic Pb at 137.6 and 142.5 eV, corresponding to the 4f_{7/2} and 4f_{5/2}, respectively. The peaks of the Pb²⁺ state with a nearly identical coordination environment only occupy a small surface area at 138.6 and 143.8 eV, which might be the result of beam damage during the measurement.³⁸ On the contrary, 3Br-2CN exhibits peaks attributed to the Pb²⁺ oxidation state.

Br 3d has two sets of binding energies, one at 67.6 eV for core species and another one at 68.6 eV for surface ions (Figure S5c).³⁹ The contribution of Br species at 68.6 eV in the composite increased, suggesting this species to be more dominant on its surface. The Cl 2p_{3/2} spectra can be deconvoluted into two sub-bands. The one at 200 eV can be attributed to the C-Cl functionalities in the sample, while the one at 197.4 eV indicates the presence of ionic chloride (Figure S5d).⁴⁰ Each set of 2p_{1/2} and 2p_{3/2} peaks is separated by a spin-orbit splitting of 1.6 eV.⁴¹

The photoreduction activities of the obtained CsPbX₃/g-C₃N₄ composites, pure CsPbBr₃, and pCN are presented in Figures 4a and S7. Control experiments to confirm the observed CO₂ reduction were performed first. In the absence of light irradiation or CO₂ (under He atmosphere) or without any photocatalyst added, no appreciable CO or other kinds of hydrocarbons were detected. In the real experiment under visible light irradiation (420–800 nm), both pure CsPbBr₃ and pCN show a similar CO production rate of about 5 $\mu\text{mol g}^{-1} \text{h}^{-1}$. The composite materials exhibit an enhanced photocatalytic activity, of which 3Br-2CN shows the best photoreduction performance with a CO production rate of

28.5 $\mu\text{mol g}^{-1} \text{h}^{-1}$, which is about 5.7 times that of pure CsPbBr₃ and 5.2 times higher than pCN. To evaluate the effect of water, a test experiment in high purity CO₂ gas without H₂O was performed. The CO amount generated after 4 h reduced by 80%, confirming the critical role of water in this photoreduction process.

For comparison, g-C₃N₄ (CN) synthesized by the traditional calcination of urea and commercial anatase TiO₂ were used as reference photocatalysts. Under visible light irradiation, the formation rate of CO over g-C₃N₄ is 4.9 $\mu\text{mol g}^{-1} \text{h}^{-1}$, in comparison to 7.1 $\mu\text{mol g}^{-1} \text{h}^{-1}$ in literature.⁴² Without the 420 nm cut-off filter, anatase TiO₂ has a CH₄ formation rate of 4.3 $\mu\text{mol g}^{-1} \text{h}^{-1}$, which is similar to the 5.9 $\mu\text{mol g}^{-1} \text{h}^{-1}$ reported.⁴³ As an additional test, we applied the precipitation method as reported in the literature⁴⁴ to synthesize the CsPbX₃/g-C₃N₄ composite with a 1:1 weight ratio of CsPbBr₃ to g-C₃N₄. This composite sample has a CO formation rate of 15.2 $\mu\text{mol g}^{-1} \text{h}^{-1}$, which is nearly half of the CO production rate obtained via the newly introduced solution-based route.

To evaluate the stability of the composites, three consecutive runs of 2 h each were performed on 3Br-2CN (Figure 4b). Only 4% activity loss was found after 6 h. Six consecutive recycling photocatalytic tests of 4 h each (in total 24 h) (Figure S8b) were further conducted on 3Br-2CN. The CO production decreased by 17% after three cycles and 50% after six cycles. To understand the stability of the composite, XRD was used. For pure CsPbBr₃, diffraction peaks of CsPb₂Br₅ could be observed after 4 h reaction, resulting from the degradation of CsPbBr₃ (shown in Figure S1b). For 3Br-2CN (shown in Figure S1c), the crystal structure was well conserved after three runs (in total 12 h); however, the decreased CO formation rate could be contributed to a gradual deactivation of the catalyst.^{45,46} After six runs, diffraction peaks of CsPb₂Br₅ appeared, explaining the substantially reduced performance.⁴⁷ XPS measurements were also performed on 3Br-2CN after six runs, but no significant difference in the XPS survey and high-resolution spectra was observed (Figures 3 and S5). For comparison, the stability test was also performed in an acetonitrile/water system according to the literature.²⁷ The composite remained stable after 6 h (Figure S8a).

To reveal the photocatalytic mechanism of the CsPbX₃/g-C₃N₄ composite, the compound surface area, the energy level

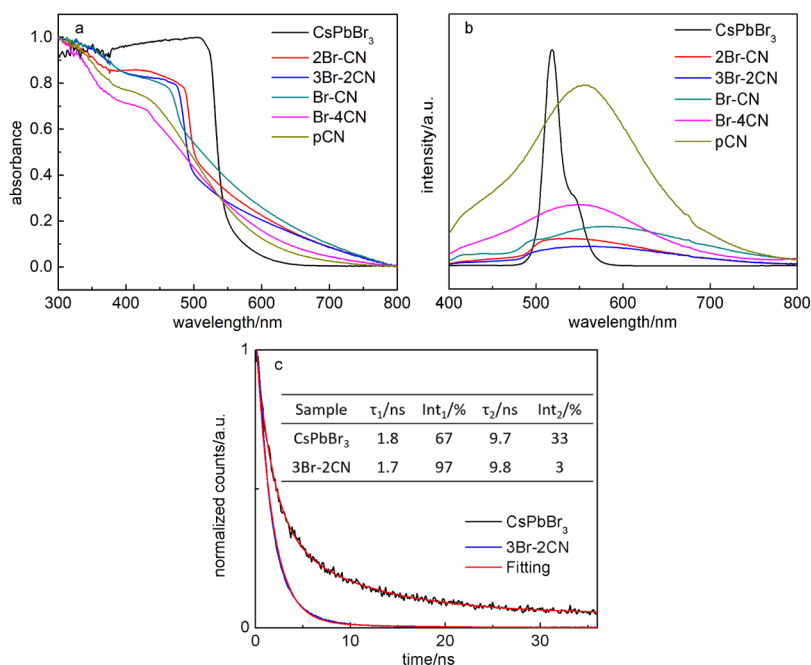


Figure 5. (a) UV-vis DRS of the as-prepared samples, (b) PL spectra at an excitation wavelength of 380 nm, (c) time-resolved PL decay signal of pure CsPbBr₃ and 3Br-2CN fitted with biexponential decay kinetics, including the corresponding fitting parameters.

of photoinduced electrons, band gap, and separation efficiency of charge carriers need to be investigated.

The specific surface areas studied by N₂ adsorption-desorption measurements (Figure S9), together with the band gap data (Figure S10a) of as-obtained samples, are listed in Table 1. From the measured surface areas, the pure CsPbBr₃ seems to be relatively compact. The introduction of g-C₃N₄ greatly increases the catalysts' specific surface area. Among all the composite samples, 3Br-2CN possesses the highest specific surface area of 68 m² g⁻¹, which favors the exposure of active sites, promotes the adsorption of CO₂ molecules, and consequently improves catalytic performance.

Normalized UV-vis diffuse reflectance spectra (DRS) of the CsPbX₃/g-C₃N₄ photocatalysts, shown in Figure 5a, were recorded to reveal the light-harvesting ability. All samples have UV and visible light response. Compared to pure CsPbBr₃, the composites show an obvious increase of absorption above 550 nm because of the introduction of g-C₃N₄. Meanwhile, the absorption edge of the CsPbBr₃ fraction shifts from about 525 nm to the lower wavelength in the composites. This blue shift is due to the Br-to-Cl anion exchange, which is also visible in the XRD patterns.^{24,31}

Photoluminescence (PL) spectra were recorded applying a 380 nm excitation. When compared to the thermal condensation way to synthesize g-C₃N₄, this solvothermal processing could improve the p-electron delocalization in the conjugated system, thus modifying the intrinsic optical property of pCN. Shown in Figure 5b, pCN has a broad peak centered at ~560 nm, which is ascribed to the intrinsic lowest unoccupied molecular orbital to highest occupied molecular orbital emission of g-C₃N₄, corresponding to its band gap. CsPbBr₃ has a peak centered at ~520 nm. The peak pattern of both CsPbBr₃ and pCN can be found in all composites. According to the literature, the Br to Cl anion-exchange would cause the gradual PL peak shift to higher energies.^{39,48} The typical PL peaks of CsPbBr₃, CsPbCl₃ and CsPbClBr₂ are positioned at 520, 457,⁴⁹ and 471 nm,⁵⁰

respectively. Thus, the ratio of Br to Cl in the composites is above 2:1.⁵¹ Clearly, PL intensity of the composites exhibits a significant decrease. Among all the composites, 3Br-2CN has the lowest intensity, indicating the effectively suppressed radiative recombination of charge carriers inside the composite system. This is beneficial because the electrons are then more available for carrying out the photocatalytic reduction.

Time-resolved PL decay curves of CsPbBr₃ and the composite 3Br-2CN were measured and fitted with a biexponential decay function (Figure 5c). The short and long PL lifetimes can be assigned to radiative and non-radiative recombination, respectively.¹⁵ The average lifetime was calculated by the following equation: $\tau_{\text{avg}} = (A_1\tau_1^2 + A_2\tau_2^2) / (A_1\tau_1 + A_2\tau_2)$ and showed an obvious decrease from 7.5 to 2.9 ns after forming the composite. According to the literature, the lifetime of CsPb(Br_xCl_{1-x})₃ only changes slightly compared to CsPbBr₃,⁵² thus, the decrease can be assigned to more effective electron extraction in the composite.⁵³

The enhanced photocatalytic performance of the CsPbX₃/g-C₃N₄ composites can be attributed to several factors. First, the introduction of g-C₃N₄ endows the composite with a large surface area and an improved light-harvesting ability above 550 nm. Second, the heterojunction is believed to create transfer pathways for the photogenerated charge carriers. In our CsPbX₃/g-C₃N₄ composites, the valence band (VB) edges of pCN, CsPbBr₃, and 3Br-2CN were estimated to be 1.55, 0.82, and 1.38 eV, respectively, by executing XPS VB spectra (Figure S10b). Taking into account the band gaps, the CB edges of the above samples are -0.8, -1.45, and -1.08 eV. Thus, the CB of the as-obtained samples are more negative than the reduction potential level of CO₂/CO (-0.53 V vs NHE). As can be seen in Figure 6, under light irradiation, photoinduced electron and hole pairs are generated and tend to migrate. Typically, the holes from the VB of g-C₃N₄ would migrate to that of CsPbBr₃, where H₂O will be trapped to generate O₂ and protons. In parallel, the electrons from the CB of CsPbBr₃ will transfer to g-C₃N₄, where the activated CO₂ can be reduced to

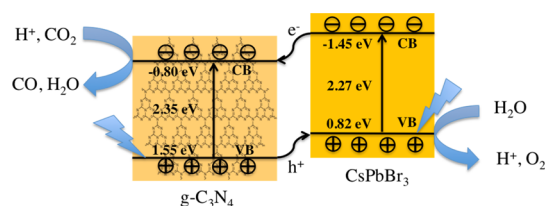


Figure 6. Schematic representation of the CO_2 photoreduction process on $\text{CsPbX}_3/\text{g-C}_3\text{N}_4$.

CO with the help of the generated protons. During the *in situ* growth of $\text{g-C}_3\text{N}_4$ in the presence of CsPbBr_3 , a considerable amount of water could soak in and accumulate on the outer surface of $\text{g-C}_3\text{N}_4$, where the water oxidation reaction could also happen. The introduction of $\text{g-C}_3\text{N}_4$ not only helps to improve the stability and performance of CsPbBr_3 but also serves as an important photocatalyst itself. The synergetic catalytic effects play an important role in the photocatalytic reaction.⁵⁴

3. CONCLUSIONS

We have successfully developed new $\text{CsPbX}_3/\text{g-C}_3\text{N}_4$ composites by a simple *in situ* solvothermal synthesis. The $\text{CsPb}(\text{Br}_x\text{Cl}_{1-x})_3$ species exhibit an homogeneous dispersion in the heterostructures. The obtained $\text{CsPbX}_3/\text{g-C}_3\text{N}_4$ composites show a significantly improved CO_2 photoreduction activity, where 3Br-2CN has the highest CO produced rate, which is about five times of that on the pure constituents. The enhanced photoactivity is mainly attributed to the enlarged surface area, increased light-harvesting capability, the efficient separation of the photogenerated charge carriers caused by the perfect matching of the band structures, and the solid bonding interfaces between CsPbBr_3 and $\text{g-C}_3\text{N}_4$. This work shows that stability engineering of perovskites by constructing perovskite-based heterostructure photocatalysts is a promising route toward exploiting the outstanding perovskite semiconductor properties in efficient solar energy conversion. Furthermore, water is an important medium involved in most of the photocatalytic reactions; thus, the stability of perovskites in aqueous solution is critical if we want to make practical use of them in photocatalysis. As compared to pure perovskites, the generation of perovskite-based composites is a step forward toward creating water-stable photocatalysts. In this context, incorporating perovskites within an ultrathin layer of graphene, within a metal-organic framework or other porous hosts, or efficient packing and subsequent shielding between appropriate hole and electron transport layers could protect them from the environment and endow them with enhanced photocatalytic performance and stability for aqueous phase photocatalysis.

4. EXPERIMENTAL SECTION

4.1. Synthesis Photocatalysts. Pure CsPbBr_3 was synthesized following an anti-solvent method reported by Huang *et al.*¹⁵ 2.5 mmol of cesium bromide (CsBr , Alfa Aesar, 99.9%) and 2 mmol of lead(II) bromide (PbBr_2 , Aldrich, $\geq 98\%$) were dissolved in 15 mL of dimethyl sulphoxide (anhydrous, VWR Chemicals, $\geq 99.9\%$) and stirred for 12 h. The solution was quickly added into 150 mL of toluene under vigorous stirring. The obtained product was collected after centrifuging and washing by toluene. After drying in the vacuum oven at 80°C , an orange-colored CsPbBr_3 powder was obtained.

Pure $\text{g-C}_3\text{N}_4$ was synthesized according to the literature.³⁰ In a typical procedure, 2 mmol of cyanuric chloride (TCI, $>97\%$) and 1 mmol of melamine (Fluka Chemika, 99%) powders were put into a 100 mL Teflon-lined autoclave filled with 60 mL of acetonitrile (anhydrous, VWR Chemicals, 99.8%). The mixture was stirred for 24 h after which the autoclave was sealed and maintained at 180°C for 12 h. The obtained product was washed with distilled water to remove residual impurities and then dried at 80°C . The sample thus obtained was named as pCN.

As a reference sample, 20 g of urea (Aldrich, $>99\%$) was placed into an alumina crucible with a cover and heated to 550°C for 2 h at a heating rate of 5°C min^{-1} .

For the $\text{CsPbX}_3/\text{g-C}_3\text{N}_4$ composites, 2 mmol of cyanuric chloride and 1 mmol of melamine powders were added into 60 mL of acetonitrile and the mixture was stirred for 12 h. Then, 0.4, 0.3, 0.2, or 0.05 g (0.7, 0.5, 0.3, or 0.1 mmol) of CsPbBr_3 was added to the precursor solution, and it was stirred for another 12 h. The mixture was transferred to an autoclave and maintained at 180°C for 12 h. The powder was washed with toluene and dried at 80°C in the vacuum oven. In the composites, the CsPbBr_3 perovskite can contain a small amount of Cl, forming a $\text{CsPb}(\text{Br}_x\text{Cl}_{1-x})_3/\text{g-C}_3\text{N}_4$ composition, shortly $\text{CsPbX}_3/\text{g-C}_3\text{N}_4$. For easy reading, the obtained samples will be further named as 2Br-CN, 3Br-2CN, Br-CN, and Br-4CN, respectively.

4.2. Characterization. XRD measurements were taken with a Stoe X-ray diffractometer using $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$). SEM images of samples were performed on a FEI-Q FEG250 microscope, equipped with an EDAX system. XPS data were recorded on an ESCALAB 250 spectrometer with a monochromatized $\text{Al K}\alpha_1$ X-rays as the excitation source. All binding energies were corrected by fitting the C 1s peak of surface adventitious carbon at 284.8 eV. The optical absorption of the samples was studied using a Lambda-950 UV-vis spectrometer. The steady-state PL spectra were recorded on an Edinburgh FLS980, under an excitation wavelength of 380 nm. Nitrogen adsorption-desorption isotherms at 77 K were carried out on a Micromeritics 3Flex surface analyzer. Before the measurement, all the samples were degassed at 130°C for 12 h under flowing N_2 . TEM images were obtained on a CM200FEG PHILIPS operated at 200 kV, equipped with an EDAX system and a GATAN Tridiem Image Filter. TGA was performed from room temperature to 800°C at a heating rate of $10^\circ\text{C min}^{-1}$ under O_2 . Fluorescence lifetime data were acquired on a home-built confocal FLIM microscope based on a single photon counting (TCSPC) device (Picoquant). The pulse frequency of the 485 nm laser diode was set at 5 MHz, and the emission was filtered by a $530 \pm 25 \text{ nm}$ bandpass filter.

4.3. Photocatalytic CO_2 Reduction Measurement. Photocatalytic reduction of CO_2 was performed in a homemade Pyrex reactor (volume: 150 mL). A 300 W Xe lamp with a 420 cut-off filter (Newport) was used as the light source and positioned 5 cm away from the photocatalytic reactor. A test sample was prepared by uniformly dispersing a 20 mg photocatalyst toluene suspension on a thin glass plate with an area of 4 cm^2 . The as-prepared sample plate was left in the vacuum oven at 80°C for 18 h to eliminate the solvent. Before the reaction, high purity helium gas first flowed through the reactor for about 20 min to eliminate the air in the reactor. The test atmosphere was a mixture of CO_2 and water vapor, generated by passing high purity CO_2 (99.99%) gas through a

water bubbler. After flowing the reactor for another 40 min with He, the measurement started under visible light (above 420 nm). After every 1 h of light irradiation, the evolved gas product was detected using a gas chromatograph (GC-2014, Shimadzu, Japan) with a thermal conductivity detector and a flame ionization detector, equipped with a ShinCarbon packed column. The carrier gas used in the GC-2014 was high purity helium. A typical GC chromatogram for the 3Br-2CN composite is depicted as Figure S6. After 24 h photostability measurement, the sample was collected and treated at 80 °C in the vacuum oven overnight.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.0c02960>.

XRD pattern of CsPbBr₃ and 3Br-2CN before and after photocatalytic reaction, SEM images and mapping of 3Br-2CN, TGA thermograms, XPS spectra, GC chromatogram of 3Br-2CN, time-dependent CO generation, stability test, N₂ adsorption-desorption analysis, and Tauc plots (PDF)

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Author Contributions

R.C. and H.J. carried out the experimental work and analysis. R.C., M.B.J.R., J.H., and E.D. designed the concept and supervised the experiments. The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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Figure 1 was incorrect in the version that published on September 16, 2020; the correct version reposted on September 17, 2020.