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A halide perovskite as a catalyst to simultaneously achieve efficient photocatalytic CO₂ reduction and methanol oxidation[†]

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A halide perovskite based photocatalyst has been demonstrated for the first time to simultaneously achieve efficient photocatalytic CO₂ reduction and methanol oxidation, exhibiting an exciting yield of 1835 µmol g⁻¹ for photocatalytic CO₂-to-CO conversion. Moreover, almost stoichiometric value-added formic acid can be produced from methanol oxidation.

The development of cost-effective artificial photosynthesis systems for the conversion of solar energy into chemical feedstocks or fuels has attracted continual interest in the last decade,¹ owing to their enormous potential to open up the possibility of a sustainable economy.² For this technology, simultaneous realization of CO₂ reduction and water oxidation without costly sacrificial agents is ultimately required for the practical application. Recently, fascinating metal-halide perovskite nanocrystals have been demonstrated to be able to achieve visible-light-driven CO₂ reduction concomitant with desirable water oxidation.3-5 Unfortunately, the practical application of metal-halide perovskite nanocrystals in the artificial photosynthesis field is limited due to their instability and inferior catalytic activity.^{6,7} In this regard, triggering meaningful chemical reactions with photogenerated holes in the catalysts is one of desirable methods to improve the economic effectiveness of photocatalytic CO₂ reduction technology.⁸ It is worth noting that metal-halide perovskite nanocrystals have also been demonstrated to be exceptional photocatalysts for fundamental organic reactions.9

Inspired by these fascinating traits of metal-halide perovskite nanocrystals, herein, we demonstrate for the first time the photocatalytic utilization of a halide perovskite for combining the reduction of CO_2 with meaningful organic reactions of methanol oxidation. Methanol is an easily available industrial chemical,¹⁰ which can be produced from both fossil resources and biomass.¹¹ The photocatalytic conversion of methanol into its downstream value-added chemical products has attracted wide attention in the last decade.^{12–15} In this study, a halide perovskite nanocomposite composed of CsPbBr₃ embedded in a Cs₄PbBr₆ matrix (coded as PNC) was prepared and used as a photocatalyst. Under the protection of wide band gap Cs₄PbBr₆, the stability of ligand-free CsPbBr₃ can be improved effectively, which has been widely demonstrated and used in optoelectronic devices.^{16–19}

The PNC and cobalt doped PNC (coded as Co@PNC) nanocomposites were synthesized according to the reported methods (Table S1, ESI †)^{17,20} with the addition of HBr to increase the solubility of CsBr, and the detailed procedures are described in the ESI.† The averaged particle sizes of PNC and Co@PNC were obtained based on transmission electron microscopy (TEM) measurements (Fig. S1, ESI⁺), being approximately 140 nm. X-ray diffraction (XRD) patterns of PNC and Co@PNC (Fig. S2, ESI[†]) just display diffraction peaks of Cs₄PbBr₆, and no characteristic peaks of CsPbBr3 can be observed, owing to the low content and small crystal size of CsPbBr3 in the Cs4PbBr6 matrix, which is consistent with previous observations.¹⁷ Furthermore, high-resolution TEM (HRTEM) measurement indicates the presence of CsPbBr₃ in the Cs₄PbBr₆ matrix (Fig. S3a, ESI[†]), exhibiting clear lattice spacings of 3.0 Å for the (002) plane of monoclinic CsPbBr₃ and 3.2 Å for the (131) plane of hexagonal Cs₄PbBr₆, respectively. TEM images (Fig. S3b, ESI⁺), elemental mappings (Fig. S3c-f, ESI⁺) and high resolution XPS spectrum (Fig. S4, ESI†) of Co@PNC indicate that Co cations are successfully implanted in the PNC with uniform dispersion.

The UV/Vis diffuse reflectance spectrum of PNC also confirms the formation of CsPbBr₃ in the Cs₄PbBr₆. As shown in Fig. 1a, apart from the absorption peak at \sim 320 nm for Cs₄PbBr₆ with a large band gap,²¹ PNC exhibits obvious absorption in the visible region with an excitonic absorption peak around 510 nm for

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Fig. 1 (a) UV/Vis diffuse reflectance spectra of PNC and Co@PNC with various doping concentrations. (b) Schematic illustration of band structures for PNC and $Co_{1\%}$ @PNC.

CsPbBr₃ in the Cs₄PbBr₆ matrix.²² Furthermore, the absorption intensity of this peak gradually increases as the feed ratio of CsBr/ PbBr₂ decreases (Fig. S5, ESI[†]), further indicating the formation of CsPbBr₃.¹⁹ In addition, doping Co in PNC with a low concentration does not obviously alter the visible light-harvesting ability (Fig. 1a). The band gaps of PNC and Co@PNC can be obtained by analyzing the Tauc plots of PNC and Co@PNC (Fig. S6a, ESI⁺), being 2.37 and 2.34 eV, respectively. On the basis of these results, the conduction band and valence band potentials of PNC and Co@PNC can be obtained in combination with the linear sweep voltammetry (LSV) measurements (Fig. S6b, ESI[†]), which are depicted in Fig. 1b. The conduction band potentials of PNC and Co@PNC are -1.18 and -1.20 V vs. NHE, respectively. In addition, the reduction potential of Co^{2+}/Co in Co@PNC can also be obtained based on the LSV measurement (Fig. S6b, ESI⁺), being -0.73 V vs. NHE. These results indicate that the photogenerated electrons in these nanocomposites have enough driving force to trigger the reaction of CO_2 reduction to $CO (-0.52 \text{ V} \nu \text{s. NHE})$.

We first evaluated the performance of photocatalytic CO_2 reduction with PNC nanocomposites as photocatalysts in a CO_2 -saturated acetonitrile/water solution. The band energy alignment of CsPbBr₃ and Cs₄PbBr₆ (Fig. S7, ESI†) with Type-I

configuration suggests that only CsPbBr₃ can produce photogenerated carriers and trigger the redox reaction under light illumination (320-750 nm), while Cs₄PbBr₆ only has a protective effect on CsPbBr₃. Illumination of this reaction system for 15 h produces only reduction product CO concomitant with negligible H₂ based on chromatographic analysis, and no liquid product can be detected. The yield of CO for this reaction system is 93 μ mol g⁻¹ (Fig. 2a). Under the same irradiation conditions, adding a small amount of methanol in the acetonitrile/H2O solution brings forth a significantly increased yield of CO, being 678 μ mol g⁻¹ (Fig. 2a), which is over 7 times higher than that of the reaction system without methanol. Moreover, liquid product HCOO⁻ can be identified by ion chromatography and mass spectra analyses in the reaction system containing methanol, and no other liquid product such as formaldehyde can be observed. In addition, to assess the protective effect of Cs₄PbBr₆ on CsPbBr₃, the performance of traditional pure CsPbBr₃ nanocrystals as photocatalysts has also been evaluated, which exhibits a very low yield of 18 μ mol g⁻¹ for photocatalytic CO₂ reduction to CO (Fig. 2a) under the same conditions. This low photocatalytic performance may originate from the inferior stability of pure CsPbBr₃ nanocrystals in the reaction containing polar solvents (Fig. S8, ESI[†]).

The cobalt doping concentration related yields of photocatalytic CO₂ reduction to CO have been further investigated in a CO₂-saturated acetonitrile/water/methanol reaction system. As presented in Fig. 2b, the yield of photocatalytic CO₂ reduction to CO can reach up to 1835 μ mol g⁻¹ by judiciously



Fig. 2 (a) The yields of photocatalytic CO₂-to-CO conversion by using PNC in the reaction system without (cyan) and with (blue) methanol, and pure CsPbBr₃ in the reaction system containing methanol (green). (b) The yields of photocatalytic CO₂-to-CO conversion by using PNC and Co@PNC with various doping concentrations as photocatalysts in the reaction system containing methanol. Irradiation condition: 15 h of irradiation under a 300 W Xe-lamp, with the light intensity of 100 mW cm⁻².

modulating the cobalt doping concentration (Co_{1%}@PNC, 0.047 wt% Co), which can be ascribed to the increased active sites (Fig. S3f, ESI⁺) and the improved efficiencies of photogenerated carrier transfer and separation (Fig. S9, S10 and Table S2, ESI[†]). These cobalt doped PNC nanocomposites exhibit a volcano-type trend of photocatalytic performance along with the increase of cobalt doping contents, which is commonly observed in the reported metal doping systems,^{20,23,24} owing to the occurrence of accelerated photogenerated carrier recombination in the case of high concentration doping. These results indicate that a suitable doping amount of Co is vital to PNC for efficient photocatalysis. Moreover, under the protection of Cs₄PbBr₆, the Co@PNC photocatalyst delivers significantly improved stability in comparsion with pure CsPbBr₃ (Fig. S8 and S11, ESI[†]). The subtle variations of the relative peak intensities in the XRD before and after the photocatalytic reaction (Fig. S11, ESI⁺) may orignate from the retention of solvent molecules and reactants in the corresponding crystal surface.²⁵

The aforementioned results of photocatalytic measurements show that liquid product HCOO⁻ can just be detected in the presence of methanol. Thereby, we preliminarily speculate that HCOO⁻ originates from methanol oxidation by consuming the photogenerated holes in these photocatalysts, while CO is generated from CO₂ reduction by consuming the corresponding photogenerated electrons. The amount of HCOO⁻ in the reaction system containing methanol has been calculated by ion chromatography measurements, and the results are tabulated in Table 1. As listed in Table 1, the results of three batches for both PNC without and with cobalt doping demonstrate their good reproducibility of photocatalytic performances. The average amount of HCOO⁻ for PNC as the photocatalyst is 1.29 µmol after 15 h of irradiation. The introduction of cobalt doping results in an obviously increased average amount of HCOO⁻, being 3.39 µmol under the same irradiation conditions, which is consistent with the changing trend of gas products. The values of consumed electrons (e⁻) and holes (h⁺) can be calculated by the equations $e^- = 2n_{CO}$ and $h^+ = 4n_{HCOOH}$, respectively, and the resultant ratios of consumed electrons and holes (e^{-}/h^{+}) are also listed in Table 1. It is clearly

Table 1	The vields c	of reduction	and	oxidation	products ^a
TUDIC 1	The yields c	reduction	unu	Oxidution	products

Sample ^b	Gas products n _{CO} [μmol]	Liquid products n _{HCOO} - [µmol]	e^{-}/h^{+c}
PNC-1	2.58	1.23	1.05
PNC-2	2.69	1.29	1.04
PNC-3	2.96	1.36	1.09
Co1%@PNC-1	7.21	3.39	1.06
Co1%@PNC-2	7.34	3.35	1.10
Co1%@PNC-3	7.28	3.44	1.06

^{*a*} Reaction conditions: 4 mg of photocatalysts were added into the mixture CO₂-saturated solution of acetonitrile (5 mL), H₂O (15 µL) and methanol (15 µL) under 300 W Xe-lamp irradiation with the light intensity of 100 mW cm⁻². Irradiation time: 15 h. ^{*b*} PNC-1, PNC-2 and PNC-3 represent three batches of PNC nanocomposites, and Co_{1%}@PNC-1, Co_{1%}@PNC-2 and Co_{1%}@PNC-3 denote three batches of cobalt doping (1%) PNC nanocomposites. ^{*c*} e⁻/h⁺ is the ratio of consumed electrons and holes in the photocatalytic reaction system, which was calculated based on the equation: e⁻/h⁺ = $2n_{CO}/4n_{HCOOH}$.

noted that the values of e^{-}/h^{+} for both photocatalysts without and with cobalt doping are close to 1, and they exhibit a good balance between CO₂ reduction and methanol oxidation.

To further clarify the origins of CO and HCOO⁻ products, we carried out a series of reference experiments by selecting Co1%@PNC as the photocatalyst in the acetonitrile/water/methanol reaction system (Table S3, ESI[†]). No gas and liquid products were produced in the absence of Co1%@PNC or light irradiation (Table S3, ESI, \dagger entries 2 and 3), indicating that the CO₂ reduction and methanol oxidation reactions are triggered by the photogenerated carriers in the Co1%@PNC. By employing Ar instead of CO₂, negligible amounts of gas product CO can be detected (Table S3, ESI[†] entry 4), which indicates that the gas product CO originates from the photocatalytic reduction of CO₂. This speculation can be further confirmed by isotope labelling experiments using ¹³CO₂ instead of CO₂. As shown in Fig. S12 (ESI^{\dagger}), the reduction product ¹³CO with the *m/z* value of 29 can be clearly identified based on the gas chromatography/mass spectrometry analysis. In addition, no ¹²CO or ¹²CO₂ can be observed in this isotope labelling experiment, ruling out the existence of methanol oxidation to CO₂ in our photocatalytic system. Moreover, the amount of liquid HCOO⁻ in the absence of CO_2 (0.13 µmol) is much lower than that observed in the presence of CO₂ (3.39 µmol). This result indicates that the presence of CO2 can accelerate the reaction of methanol oxidation by consuming the photogenerated electrons in Co_{1%}@PNC to abate the recombination of photogenerated carriers. Vice versa, the photocatalytic CO₂ reduction can be accelerated along with the introduction of methanol by consuming the photogenerated holes (Fig. 2a, Table S3, ESI[†] entry 5). In addition, when CH₃OH was replaced with benzyl alcohol (Table S3 (ESI⁺), entry 7), a smaller amount of CO was detected, indicating that CH₃OH is more easily oxidized as an electron sacrificial reagent. Moreover, both Cs₄PbBr₆ and Co²⁺ ion doped Cs₄PbBr₆ were inactive in the photoreaction system (Table S3 (ESI⁺), entries 8 and 9), indicating the merely protective effect of Cs₄PbBr₆ on the CsPbBr₃.

It is known that HCOO⁻ is also one of common reduction products of photocatalytic CO₂.²⁶ To further confirm the origin of liquid product HCOO⁻, isotopic ¹³CO₂ and ¹³CH₃OH have been employed to conduct the photocatalytic reaction, respectively, and ¹³C NMR measurements were carried out to identify the corresponding liquid products. As presented in Fig. 3a, apart from the characteristic peaks corresponding to CD₃CN (117.91 ppm and 0.90 ppm), only a peak at 125.36 ppm can be detected in the ^{13}C NMR spectra of the product generated from the photocatalytic reaction with ¹³CO₂ and CH₃OH as feedstocks, which can be assigned to dissolved ¹³CO₂ in CD₃CN. When CO₂ and ¹³CH₃OH were employed as feedstocks, the result of the ¹³C NMR spectra analysis can clearly identify the liquid product HCOO⁻ featuring a characteristic peak at 163.57 ppm (Fig. 3b). Thereby, we can confirm that the liquid product HCOO⁻ is produced by the oxidation of methanol rather than the reduction of CO₂. Finally, the photocatalytic mechanisms for the photoredox reactions are proposed in Fig. S13 (ESI⁺) according to previous reports. For CO₂ reduction, initially, the cobalt ions on Co@PNC could fix CO2 and undergo a proton-coupled electron transfer (PCET) and the



Fig. 3 The ^{13}C NMR spectra for the products obtained from the reaction with (a) $^{13}\text{CO}_2$ and CH_3OH and (b) CO_2 and $^{13}\text{CH}_3\text{OH}$ as feedstocks by using Co_{1%}@PNC as the photocatalyst.

cleavage of the C–OH bond within Co-COOH to generate CO.²⁷ For methanol oxidation, methoxy radicals and formaldehyde may be the intermediates, which can be further oxidized to yield HCOOH with the photogenerated holes.²⁸

In summary, we have elaborately constructed a highly efficient photocatalytic system for CO₂-to-CO conversion by employing CsPbBr₃/Cs₄PbBr₆ nanocomposites as photocatalysts. The introduction of methanol in the reaction system can significantly improve the performance of photocatalytic CO₂ reduction by accelerating the rate of hole consumption, achieving an extremely high yield of 1835 µmol g⁻¹ for the reduction of CO₂ to CO. Moreover, further characterization of the liquid phase product has confirmed that methanol is oxidized into high value-added formic acid. This work is the first demonstration that halide perovskite nanocrystals can achieve highly efficient photocatalytic CO₂ reduction integrated with an oxidizing organic substrate into a value-added product, which provides a fascinating solution for the further design of cost-effective CO₂ reduction systems and boost their practical applications for efficient solar-to-fuel conversion.

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Conflicts of interest

There are no conflicts to declare.

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