Mechanochemically synthesized Pb-free halide perovskite-based Cs$_2$AgBiBr$_6$–Cu–RGO nanocomposite for photocatalytic CO$_2$ reduction†

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Pb-based halide perovskites have recently showed great potential in various applications such as solar cells, optoelectronics and photocatalysis. Despite their high performance, the Pb$^{2+}$ toxicity along with poor stability hinders long term applications in photocatalysis. Herein, we report mechanochemically prepared Pb-free Cs$_2$AgBiBr$_6$ double perovskite nanoplates and their heterostructure with Cu-loaded reduced graphene oxide (Cu–RGO) for gas-phase photocatalytic CO$_2$ reduction using water vapor as the proton source in the absence of a hole scavenger. The resulting Cs$_2$AgBiBr$_6$–Cu–RGO nanocomposite shows significant photocatalytic activity of 10.7 (±0.6) μmol CH$_4$ g$^{-1}$ h$^{-1}$, 1.9 (±0.3) μmol CO g$^{-1}$ h$^{-1}$ and 1.0 (±0.2) μmol H$_2$ g$^{-1}$ h$^{-1}$, with a CH$_4$ selectivity of 93.0 (±0.5)% on an electron basis with 1 sun and a remarkable apparent quantum efficiency of 0.89 (±0.21)% at 590 nm. A further 32% enhancement in photocatalytic activity on an electron basis is achieved when the light intensity is doubled (2 suns). The high performance was attributed to their improved charge separation and suppressed electron–hole recombination, along with extended visible light absorption, better stability in a humid environment and improved CO$_2$ adsorption. These findings support Cs$_2$AgBiBr$_6$ as a potential Pb-free alternative to conventional halide perovskites for photocatalytic solar-to-fuel conversion and CO$_2$ utilization.

Introduction

Semiconductor photocatalysis has attracted great attention in recent years for various applications such as organic synthesis, pollutant degradation, N$_2$ fixation, H$_2$ production, and CO$_2$ reduction. In particular, photocatalytic CO$_2$ reduction, so-called “artificial photosynthesis”, has the potential to produce carbon-based value-added fuels and chemicals as sustainable feedstocks for the chemical industry. This photocatalysis technology provides promising and viable routes to both tackle global climate change and deliver on renewable energy demand. Among different photocatalytic materials, halide perovskites have recently emerged as new potential candidates for photocatalytic energy applications such as H$_2$ production and CO$_2$ reduction, due to their tuneable bandgap, high absorption coefficient and high carrier mobility. For example, in recent years, the all-inorganic perovskite CsPbBr$_3$ has greatly attracted attention for photocatalytic CO$_2$ reduction. Hou et al. prepared CsPbBr$_3$ quantum dots for photocatalytic reduction of CO$_2$ to CO and CH$_4$, with a production of 4.3 and 1.5 μmol g$^{-1}$ h$^{-1}$, respectively. Furthermore, CsPbBr$_3$-based composites such as CsPbBr$_3$ quantum dots (QD)-reduced graphene oxide (RGO), CsPbBr$_3$ QD-ZIF-67, CsPbBr$_3$–Cu–RGO nanocomposite shows improved CO$_2$ photoreduction to CH$_4$ with a selectivity of 98.5% on an electron basis and a remarkable apparent quantum efficiency of 1.1% at 523 nm with water as a proton source. Unfortunately, the well-known toxicity of Pb cations does not comply with sustainable design principles, hampering their development and application.

Recently, lead-free halide perovskites have been studied to overcome the toxicity challenge. Examples include Cs$_5$SnX$_{3n}$, CsSbX$_3$ and various double perovskites (A$_2$BB’X$_6$). In particular Cs$_2$AgBiBr$_6$, with a band gap of 1.8–2.2 eV and a long carrier recombination lifetime, has shown better stability toward moisture, air, heat and light when compared to other Pb-
free double perovskites.11 Because of this, bulk Cs₂AgBiX₆ (X = Cl, Br) has been studied to understand its intrinsic properties from both an experimental and a theoretical point of view.23 Very recently, Cs₂AgBiX₆ showed its potential for application in photocatalytic H₂ production,24 CO₂ reduction25,26 and dye degradation.27 For example, Zhou et al. prepared Cs₂AgBiBr₆ double perovskite nanocrystals with cubic shape via a solution-phase hot injection method. These nanocrystals showed an activity of 2.35 μmol g⁻¹ h⁻¹ CO and 1.6 μmol g⁻¹ h⁻¹ CH₄ (both products on electron consumption basis) for the CO₂ reduction reaction under simulated solar light, using ethyl acetate as both the solvent and proton source.25 The disadvantages of such a proton source are its high cost and the misleading formation of CO through oxidation.26 Therefore, it is vital to develop the use of water as a proton source and an organic-free medium for a sustainable application.

In this work, we have successfully prepared Cs₂AgBiBr₆ nanoplates and their nanocomposites with Cu–RGO by an efficient, scalable and reproducible mechanochemical method. More importantly, we further tested them for gas-phase photocatalytic CO₂ reduction to CH₄ (major) and CO (minor) with H₂O vapor as a proton source in the absence of organic solvents, under simulated sunlight. The Cs₂AgBiBr₆–Cu–RGO heterostructure photocatalyst showed significant improvement when compared to the pristine double perovskite nanoplates. The photocatalytic CO₂ reduction achieved 10.7 (±0.6) μmol CH₄ g⁻¹ h⁻¹ and 1.9 (±0.3) μmol CO g⁻¹ h⁻¹ and 93.0 (±0.5)% CH₄ selectivity, along with an apparent quantum efficiency of 0.89 (±0.21)% at 590 nm.

**Experimental details**

**Materials and methods**

CsBr (99.9%, Acros Organics), AgBr (99%, Sigma-Aldrich), BiBr₃ (99%, Sigma-Aldrich), Cu(NO₃)₂·3H₂O (99%, Sigma-Aldrich), ethylene glycol (99%, Acros Organics), tetrabutylammonium hexafluorophosphate (98%, Sigma-Aldrich), acetonitrile (99.9%, Sigma-Aldrich) and isopropanol (99.7%, VWR Chemicals) used in this work are of analytical grade and used as received. Cs₂AgBiBr₆ nanoplates were synthesized by mechanochemical synthesis. In detail, 2 mmol of CsBr, 1 mmol of AgBr, and 1 mmol of BiBr₃ were added to a 45 mL zirconia bowl containing 180 zirconia balls of 5 mm under an Ar atmosphere in a glovebox (<0.5 ppm H₂O, <0.5 ppm O₂). The gas-tight zirconia bowl with zirconia balls and Cs, Ag and Bi bromide precursors was then placed in a ball mill (Planetary Mono Mill Pulverisette, Fritsch) and milled at 500 rpm for 60 min. This was the optimal time to achieve good crystallization and avoid excessive sintering. The as-prepared Cs₂AgBiBr₆ nanoplates were collected and stored in the glovebox.

Graphene oxide (GO) was prepared by using a modified Hummer’s method previously reported by our group.28 RGO and Cu–RGO were prepared as we previously described.28 Briefly, a mixture of Cu(NO₃)₂·3H₂O and GO was reduced in ethylene glycol at 180 °C for 24 h. Different Cu loading of 1, 3, 5, 7 and 10 wt% Cu–RGO were prepared by varying the amount of Cu(NO₃)₂·3H₂O. Actual loadings determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) were 0.94, 3.06, 4.91, and 9.87 wt%. RGO was synthesized in the same manner from GO, just without the addition of Cu(NO₃)₂·3H₂O.

Composites of Cs₂AgBiBr₆ and either Cu–RGO or RGO were prepared by adding 5 mL of either Cu–RGO or RGO isopropanol suspensions (2.4 mg mL⁻¹) to the mixture of precursors before ball milling. RGO was approximately 1 wt% in all the Cs₂AgBiBr₆–RGO composites, which is known to be optimal in RGO-photocatalyst composites.29 A physical mixture of Cs₂AgBiBr₆ and Cu–RGO was also prepared by simply mixing the powders in the same mass ratio. Cs₂AgBiBr₆ is sometimes abbreviated in legends as DP for double perovskite.

**Characterization**

Powder X-ray diffraction (XRD) was carried out in a Bruker-AXS D8 ADVANCE diffractometer operated at 40 kV voltage and 40 mA current using Cu Kz (λ = 0.15418 nm) radiation in the 2θ range 5–70°. The coherent diffraction domain size of Cs₂AgBiBr₆ was calculated using the Scherrer equation on the 022, 004, and 044 diffraction peaks. X-ray photoelectron spectroscopy (XPS) analysis was done using a Kratos Axis HSI spectrometer and monochromated Al Kz X-ray source operated at 90 W. Furthermore, the binding energies were referenced relative to adventitious carbon at 284.6 eV. The XPS data were processed using CasaXPS version 2.3.16. The same XPS tool was used to carry out ultraviolet photoelectron spectroscopy (UPS). The morphology and crystallinity of the as-prepared samples were examined by high-resolution transmission electron microscopy (HRTEM) using a JEOL JEM-2100Plus microscope operating at an accelerating voltage of 200 kV. The surface mapping analysis was done using energy dispersive X-ray spectroscopy (EDX) with an Oxford INCA X-ray analyzer. Light absorption of the as-prepared samples was measured by UV-visible diffuse reflectance spectroscopy (UV-Vis DRS) on a Cary 100 spectrophotometer (Agilent Technologies) using an integrating sphere for diffuse reflectance and KBr as a standard. The baseline was corrected using pure KBr and then 10 mg of sample were mixed with KBr for analysis. Furthermore, the band gap energy (Eₚ) of all the Cs₂AgBiBr₆ samples was determined using Tauc plots of [F(R)hv]² versus hv and drawing a tangential line at the onset of the linear response,28 where F(R), hv, and η are the Kubelka–Munk function, energy of light, and a variable that depends on the nature of the optical transition during photon absorption (equal to 2 in this case), respectively. F(R) was calculated as F(R) = [(1 – R)²/(2R)]⁻¹, where R is the reflectance of the sample.28 The phospholinescence (PL) emission kinetics of powder samples were measured on a DeltaFlex TCSPC equipment (Horiba Scientific). The samples were excited by using an LED at 470 nm (Horiba NanoLED) and the photons were detected with a photomultiplier detector (Horiba PPD-650). Each PL spectrum was individually normalized by the mass of the sample. Photocurrent measurements were carried out in a three-electrode PEC cell with quartz window, working electrode, Pt wire counter electrode, Ag/AgCl reference electrode, and 0.1 M tetrabutylammonium hexafluoro-phosphate in acetonitrile as electrolyte solution. A 300 W Xe lamp equipped
with an AM1.5G solar simulator filter (LOT Quantum Design) was used with 100 mW cm\(^{-2}\) (1 sun) determined by the distance to the working electrode and this was chosen with an automatic shutter. An external potential of 0.0 V vs. Ag/AgCl reference electrode was applied with a potentiostat (Ivium CompactStat). Working electrodes were prepared by spin coating on fluorine-doped tin oxide coated glass the Cs\(_2\)AgBiBr\(_6\) samples previously dispersed in dimethyl sulfoxide. Nitrogen and CO\(_2\) adsorption measurements were carried out with a Quantachrome Autosorb IQ\(_3\) porosimeter. Surface areas were calculated over the nitrogen relative pressure range 0.01–0.2 using the Brunauer–Emmett–Teller (BET) model.

**Photocatalysis**

Photocatalytic CO\(_2\) reduction experiments of the as-prepared powder photocatalysts were carried out at room temperature in a gas-tight 125 mL glass photoreactor with a top quartz light window. The light intensity at the photocatalyst surface was adjusted to 1 sun (100 mW cm\(^{-2}\)) using an AM1.5G mass filtered 300 W Xe source at an appropriate distance. 50 mg of powder sample were placed in a glass holder within the photoreactor. Prior to irradiation, the reactor was purged with He gas to remove air from the system and then purged with CO\(_2\) for 1 h at 5 mL min\(^{-1}\) and humidified by injecting water at 1 mL h\(^{-1}\) simultaneously with a high-precision pump. The observed relative humidity was 60–65%, measured by a dew point meter HT-6292 from Landtek. Finally, the gas inlet and outlet in the reactor were closed before the CO\(_2\) reduction experiments were carried out for 1 h under 1 sun. The formed products were analyzed by gas chromatography (GCMS, Shimadzu GC-2030 Plus) with He as a carrier gas and a barrier ionization discharge (BID) detector. Reusability experiments were carried out for three successive experimental runs on the used powder sample by each time degassing with He, followed by purging with fresh CO\(_2\) and water, and then irradiating for 4 h (12 h of total irradiation) under 1 sun. The error bars in graphs or ± symbol in the text indicate standard deviation. The selectivity (S) of the obtained products was calculated on a total electron consumption basis as given in the following equations:\(^\text{31,32}\)

\[
S_{\text{CO}} (\%) = \frac{2N_{\text{CO}}}{8N_{\text{CH}_4} + 2N_{\text{CO}} + 2N_{\text{H}_2}} \times 100
\]

\[
S_{\text{CH}_4} (\%) = \frac{8N_{\text{CH}_4}}{8N_{\text{CH}_4} + 2N_{\text{CO}} + 2N_{\text{H}_2}} \times 100
\]

\[
S_{\text{H}_2} (\%) = \frac{2N_{\text{H}_2}}{8N_{\text{CH}_4} + 2N_{\text{CO}} + 2N_{\text{H}_2}} \times 100
\]

where \(N_{\text{CH}_4}\), \(N_{\text{CO}}\), and \(N_{\text{H}_2}\) are the production rates of CH\(_4\), CO, and H\(_2\) in \(\mu\text{mol g}^{-1} \text{ h}^{-1}\) and the coefficients 8, 2 and 2 are used to account for the total electrons involved in the CO\(_2\) or H\(_2\)O reduction to form CH\(_4\), CO and H\(_2\), respectively. The apparent quantum efficiency (AQE) was measured using the same experimental conditions, but with 590 nm LED light and the following equation used for the calculations:

\[
\text{AQE} (\%) = \frac{\text{Number of reacted electrons} \times 100}{\text{Number of incident photons}}
\]

Further details of the AQE calculations were given in a previous publication.\(^\text{18}\)

### Results and discussion

A surfactant/ligand-free mechanochemical strategy was used to prepare Cs\(_2\)AgBiBr\(_6\) nanocrystals and their Cu–RGO composites (Scheme 1). The kinetic energy of the balls is transferred to Cs, Ag and Bi bromide precursors during the milling process, allowing the collision between reactant molecules which then result in a chemical reaction to form Cs\(_2\)AgBiBr\(_6\) nanocrystals, as shown below:\(^\text{19}\)

\[
2\text{CsBr} + \text{AgBr} + \text{BiBr}_3 \rightarrow \text{Cs}_2\text{AgBiBr}_6
\]

![Scheme 1](image-url)  
**Scheme 1** Schematic diagram of the Cs\(_2\)AgBiBr\(_6\) nanoplades and Cs\(_2\)AgBiBr\(_6\)–Cu–RGO nanocomposites by a surfactant/ligand-free mechanochemical synthesis method.
The morphology and crystal structure were examined by TEM and HRTEM. Cs₂AgBiBr₆ nanocrystals show nanoplate, that is slab shape, with a thickness of 80–100 nm and a lateral size of a few hundred nm (Fig. 1a). HRTEM lattice fringes show an interplanar spacing of 0.29 nm which is assigned to the 004 plane of the Cs₂AgBiBr₆ phase (Fig. 1b). A selected angle electron diffraction (SAED) pattern further confirms their crystallinity and pure Cs₂AgBiBr₆ phase (Fig. S1†). The as-prepared RGO shows a layered structure with typical wrinkled surfaces of re-stacked nanosheets due to van der Waals (vdW) interlayer interactions in dried samples (Fig. S2a†). After decorating the surface with Cu nanoparticles (Cu–RGO), the typical wrinkled surface remains unchanged but a rougher surface can be appreciated (Fig. S2b†). The size range of uniformly dispersed Cu nanoparticles is 3–5 nm. More interestingly, after hybridising Cs₂AgBiBr₆ (DP) with Cu–RGO, the Cs₂AgBiBr₆ nanoflakes appear to be highly dispersed on the Cu–RGO and show relatively smaller dimensions, with a thickness of 20–40 nm and lateral size of 60–70 nm (Fig. 1c and S2c†). HRTEM micrographs also show intimate contact between the Cs₂AgBiBr₆ nanoflakes and Cu–RGO (Fig. 1d) and clear lattice fringes for both Cs₂AgBiBr₆ (Fig. 1e) and Cu (Fig. 1f). Furthermore, EDX mapping confirms the ubiquitous presence of Cs, Ag, Bi, Br, Cu and C in DP–Cu–RGO (Fig. S3f). The percentage of Cu is 0.25 wt% as calculated by EDX, whereas RGO is 1 wt% based on the loaded amount during mechanochemical synthesis.

XRD patterns of Cs₂AgBiBr₆ nanoplates, DP–RGO and DP–Cu–RGO samples are given in Fig. 2a. The obtained XRD pattern of Cs₂AgBiBr₆ (DP) shows its characteristic diffraction peaks at 12.8, 15.1, 22.2, 25.1, 26.0, and 31.8° (2θ), corresponding to the 111, 200, 022, 311, 222, 400 and 044 planes, respectively (JSPCDS #01-084-8699). This indicates that Cs₂AgBiBr₆ consists of a cubic structure with a = 11.271 Å and space group symmetry Fm3m, which accounts for the Bi/Ag ordering in a rock-salt-like superstructure. The calculated coherent diffraction domain size is 107 (±5) nm, similar to their physical thickness (120–170 nm). Both DP–RGO and DP–Cu–RGO composites show the same cubic Cs₂AgBiBr₆ DP crystal phase in the XRD patterns, indicating that the type of phase is not affected by the addition of RGO or Cu–RGO under the chosen synthesis conditions. However, the calculated coherent diffraction domain size of Cs₂AgBiBr₆ is reduced to 52 (±5) nm in DP–Cu–RGO.

UV-Vis DRS spectra of Cs₂AgBiBr₆, RGO, and DP–Cu–RGO nanocomposites are shown in Fig. 2b. The spectrum of Cs₂AgBiBr₆ shows a broad absorption starting around 600 nm in the visible region, corresponding to an indirect band gap of 2.0 eV (Fig. S4a†). The DP–Cu–RGO nanocomposite shows a similar absorption onset attributed to the Cs₂AgBiBr₆, but an upward shift in the absorption baseline due to the presence of Cu–RGO (Fig. S4b†), since this absorbs broadly in the UV-Vis region (Fig. 2b).

XPS was used to probe the chemical oxidation state of Cu, Cs, Ag, Bi and Br and their chemical environment (Fig. 3a–d and S5†). Compared to DP, the Cs 3d, Ag 3d, Bi 4f and Br 3d peaks of DP–Cu–RGO show lower intensity, suggesting the DP in DP–Cu–RGO is partially wrapped by RGO (Fig. 3a, b, S5c and d†). Further, Ag 3d spectra of DP–Cu–RGO exhibit two extra spin–orbit doublets at 368.3 eV and 374.4 eV related to Ag–O bond.

Fig. 1 TEM and HRTEM micrographs of (a and b) DP and (c–f) DP–Cu–RGO.

Fig. 2 (a) XRD patterns and (b) UV-Vis DRS spectra of Cs₂AgBiBr₆ (DP) and DP–Cu–RGO nanocomposite among others for comparison. Inset in (b) shows photographs of DP, Cu–RGO and DP–Cu–RGO from left to right.
568.3, 568.8, and 570.2 eV, corresponding to Cu, CuO, and Cu2O, which deconvolutes into three peaks with binding energy of electronic work function, valence band edge and conduction band edge, respectively.

These results indicate that the perovskite is at least in part anchored to RGO via bonds between the metals (Ag and Bi) in the perovskite octahedra and residual O-groups on RGO. The O 1s spectrum of DP–Cu–RGO is deconvoluted into three peaks centered at 532.0, 530.3, and 529.3 eV (Fig. 3c). These are attributed to residual C–OH in RGO, residual C=O or O=C=O in RGO, and Ag–O/Bi–O bonds, respectively.36,38 Cu LMM spectra shows a peak just below 570 eV in DP–Cu–RGO composites, which deconvolutes into three peaks with binding energy of 568.3, 568.8, and 570.2 eV, corresponding to Cu, CuO, and Cu2O (Fig. 3d).39

Valence-band (VB) XPS was used to determine the energy gap between the VB edge potential and the Fermi level (Fig. 3e, f). The calculated value from the intercept between the tangent of the onset and the baseline of the spectra is approximately 1.4 eV, which is consistent with reported VB energy values.32 Furthermore, UPS served to measure the electronic work function, i.e., the difference between ET and the vacuum level, found to be 4.3 eV (Fig. 3f). With this information and the band gap value from UV-Vis DRS (2.0 eV), we constructed the electronic band diagram of Cs2AgBiBr6, as shown in Fig. 3g. The resulting CB edge potential is at −3.7 eV from the vacuum level (−0.6 V_NHE at pH = 7). This indicates that Cs2AgBiBr6 possesses a suitable CB edge potential for multielectron CO2 reduction to low carbon products such as CO (CO2/CO, −0.53 V_NHE at pH = 7) and CH4 (CO2/CH4, −0.24 V_NHE at pH = 7).

PL emission spectra were recorded for DP and DP–Cu–RGO to understand the charge carrier dynamics between phases (Fig. 4a). DP exhibits a wide typical PL peak around 600 nm (2.0 eV) and an additional peak around 670 (1.85 eV), corresponding to indirect band gap transitions of Cs2AgBiBr6.7,40 The normalized PL intensity of the DP–Cu–RGO nanocomposite is much lower than that of DP, which can be attributed to suppressed electron–hole recombination and photoinduced charge carrier separation between Cs2AgBiBr6 and Cu–RGO. Furthermore, time-resolved PL measurements were carried out to confirm the charge transport behavior on DP–Cu–RGO nanocomposites (Fig. 4b). Average charge carrier lifetimes (τav) were determined from fitting the resulting decay curves with a three-exponential function (Table S1†), consistent with three decay processes, such as nonradiative and radiative relaxations originating from the direct formation of free charge carriers and the indirect formation of self-trapped excitons.13 DP–Cu–RGO showed lower τav values than DP (0.2 vs. 1.5 ns), which indicates the presence of a nonradiative pathway that suppresses electron–hole pair recombination and thereby improves charge carrier separation. This electronic transport behavior further confirms an excellent interface at the heterostructure between the DP and Cu–RGO. Further, this is supported by photocurrent measurements on samples mounted on electrodes. The DP and DP–Cu–RGO electrodes exhibit a photocurrent response to on–off cycles under light irradiation with a bias of 0 V vs. Ag/AgCl. Interestingly, the DP–Cu–RGO based electrode exhibits much higher photocurrent response than that of DP–RGO and DP (Fig. 4c), consistent with the better charge separation observed by PL.

N2 adsorption–desorption on Cs2AgBiBr6 (DP), DP–RGO, DP–Cu–RGO, and a physical mixture of DP and Cu–RGO was carried...
out to study their surface area (Fig. 5a). All the samples show typical type II isotherms with type III hysteresis which are characteristic of non-porous materials and slit-like pores, which might be due to interparticle porosity. The DP–Cu–RGO nanocomposite shows relatively higher BET surface area (82 m² g⁻¹) than Cs₂AgBiBr₆ nanoplates (62 m² g⁻¹), due to the presence of RGO, a two-dimensional material, and observed smaller DP particles in the composite (Fig. 1c–e). The BET surface area of DP–RGO is similar to that of the DP–Cu–RGO nanocomposite (77 vs. 82 m² g⁻¹). It is worth noting that the BET surface area of DP–Cu–RGO is larger than the physical mixture of DP and Cu–RGO (72 m² g⁻¹), indicating that the Cu–RGO presence during the mechanochemical synthesis has a templating effect increasing the surface area of the composites. In addition, CO₂ physisorption was also carried out, as CO₂ adsorption is the first and a key step in photocatalytic CO₂ reduction (Fig. 5b). The CO₂ physisorption of DP–Cu–RGO (5.2 cm³ g⁻¹) is relatively higher than that of DP (4.2 cm³ g⁻¹), physical mixture of DP and Cu–RGO (4.7 cm³ g⁻¹), and DP–RGO (3.8 cm³ g⁻¹), in agreement with the trends observed in BET surface area.

To test their thermal stability, 100 mg of the as-prepared Cs₂AgBiBr₆ DP nanoplates were placed in an alumina crucible and heated to 100 and 300 °C for 1 h in an oven under ambient conditions (air with relative humidity 60–70%, Fig. S6f). Upon heating, no additional diffraction related to the formation of secondary phases such as Cs₃Bi₂Br₇ or AgBr is observed, just narrowing of the XRD peaks due to sintering. These results show the high thermal stability of Cs₂AgBiBr₆ DP nanoplates, like CsPbBr₃ and unlike organic–inorganic halide perovskites. Regarding long-term ambient stability at room temperature and ambient conditions with relative humidity 60–70%, pure Cs₂AgBiBr₆ nanoplates are stable for at least two days, but decompose to AgBr, Cs(OH)₂ and Cs₂Bi₂Br₆ after 8 days (Fig. S7f). Interestingly, the DP–Cu–RGO composite showed relatively higher stability under the same environment and no phase change even after 8 days (Fig. S8f), with only nanoparticle sintering observed over time. The high stability of the DP–Cu–RGO composite under 60–70% relative humidity ambient conditions indicates that the RGO, of more hydrophobic character, acts as a protection layer for the Cs₂AgBiBr₆ DP.

The photocatalytic CO₂ reduction with water vapor as a proton source on all the samples was carried out under simulated solar light (1 sun, Fig. 6a–d). The photocatalytic activity of Cs₂AgBiBr₆ nanoplates (DP) is 1.49 (±0.09) μmol CH₄ g⁻¹ h⁻¹, 0.54 (±0.03) μmol CO g⁻¹ h⁻¹ and 0.19 (±0.01) μmol H₂ g⁻¹ h⁻¹. This is relatively lower than conventional all-inorganic CsPbBr₃ halide perovskite nanocrystals prepared by mechanochemical synthesis and tested in the same photocatalytic reactor (Fig. 6a and b). This can be attributed to the indirect band gap of Cs₂AgBiBr₆, compared with the direct band gap of CsPbBr₃, despite being smaller (Fig. S9f). Interestingly, DP–RGO shows twice the activity of DP, something that was not achieved previously in CsPbBr₃–RGO (Fig. 6c and d). We anticipate that this could be due to the presence of Ag–O and Bi–O between Cs₂AgBiBr₆ and RGO which can help in fast transfer of holes and thereby water oxidation. More importantly, the
composite DP–Cu–RGO shows remarkable photocatalytic activity of 10.7 (±0.6) μmol CH4 g⁻¹ h⁻¹, 1.9 (±0.3) μmol CO g⁻¹ h⁻¹ and 1.0 (±0.2) μmol H2 g⁻¹ h⁻¹, much higher than that of pure Cs₂AgBiBr₆ nanoplates, DP–RGO and Cu–RGO (Fig. 6c and d). RGO was approximately 1 wt% in all the Cs₂AgBiBr₆–RGO composites, which is known to be optimal in RGO-photocatalyst composites. The optimum DP–Cu–RGO composite contains 1 wt% Cu–RGO content with an optimal 5 wt% of Cu content in Cu–RGO (Fig. S10a†). A further increase of Cu content in Cu–RGO suppressed the photocatalytic activity for CO₂ reduction, assigned to an increased Cu particle size and poorer dispersion. The CH₄ selectivity also increases for DP–Cu–RGO compared with DP, from 46.0 (±0.5) to 93.0 (±0.5)%.

Overall, the photocatalytic activity of DP–Cu–RGO, on a total electron (e⁻) consumption basis is 93 μmol e⁻ g⁻¹ h⁻¹ with 1 sun, which is almost 13 times higher than that of pure DP (7 μmol e⁻ g⁻¹ h⁻¹). Further, a 32% enhancement in photocatalytic activity is observed on electron consumption basis when light intensity is doubled (2 sun). However, selectivity of CH₄ decreased (18%) as more H₂ evolution is observed (Fig. 7a). We attribute this to the heat generated under concentrated light, changing the adsorption of H₂O and CO₂ on the photocatalyst surface (the reactor temperature was 22 and 39 °C under 1 and 2 sun, respectively).

Based on our findings, this remarkable improvement in photocatalytic activity can be attributed to the enhanced charge separation and suppressed recombination of electron–hole pairs in the closely interfaced DP–Cu–RGO composites, along with higher light absorption and CO₂ adsorption. Furthermore, the relatively very low photocatalytic activity of a physical mixture of Cs₂AgBiBr₆ nanoplates and Cu–RGO (manually mixed powder samples) confirms our argument (Fig. 6c). The total O₂ evolved on both pure composite photocatalysts was consistent with a CH₄ : O₂ and (CO + H₂) : O₂ theoretical stoichiometry of 1 : 2 and 2 : 1, respectively, and with the actual involvement of 4, 8, 2 and 2 e⁻ to form O₂, CH₄, CO and H₂, respectively. Hence, photocatalytic CO₂ conversion to CH₄ (and minor CO and H₂) by using water vapor as a proton source was achieved without a hole scavenger such as an alcohol. Furthermore, the apparent quantum efficiency (AQE) for CH₄ production on DP–Cu–RGO is found to be 0.89 (±0.21)% at 590 nm, which is interestingly very close to the AQE of CsPbBr₃–Cu–RGO (1.1% at 523 nm) and much higher than other efficiencies reported for similar heterogeneous photocatalysts (Table S2†). Therefore, Cs₂AgBiBr₆ could be a potential safer alternative to CsPbBr₃ containing toxic Pb²⁺. We also carried out various control experiments on pure Cs₂AgBiBr₆ nanoplates and DP–Cu–RGO composite in the absence of CO₂, H₂O, photocatalyst or light irradiation, and confirm that the carbon source is CO₂ (Fig. S10b and c†). This was further supported by ¹³CO₂ experiments using GCMS (Fig. S11†). Hence, we confirm that there was no involvement of a secondary carbon source from
organic contamination in the photocatalytic production of CO and CH₄ in this work.⁶⁷,⁶⁸ Finally, we examine the recyclability of the pure Cs₂AgBiBr₆ nanoparticles and DP–Cu–RGO composite by evacuation and refilling of the reactor with a fresh CO₂ and water vapor mixture for three successive times. The photocatalytic activity of the Cs₂AgBiBr₆ nanoparticles drops drastically during the three cycles (Fig. S12†), whereas the DP–Cu–RGO composite continued to produce similar activity even on the third cycle (Fig. 7b). This is attributed to the improved chemical stability of DP–Cu–RGO due to its RGO content (see previous stability tests in Fig. S7 and S8†). As shown in Fig. S13 and S14,† there is no change in the crystal structure and morphology of DP–Cu–RGO after the three photocatalytic cycles, while DP undergoes phase change as well as decomposition to AgBr and Cs(OH)₂.

Photocatalytic CO₂ reduction over DP–Cu–RGO is proposed as shown in Fig. 7c. Briefly, upon light irradiation, photoinduced electrons are promoted to the conduction band of the Cs₂AgBiBr₆ with band gap of 2.0 eV and then migrate through the DP–Cu–RGO heterostructure, eventually reaching the Cu nanoparticles.⁴⁹ There, CO₂, either weakly chemisorbed directly at the Cu surface or spilled over onto Cu facets in contact with the RGO support, undergoes reduction, likely via the activated CO₂ in a multi proton-coupled process (Fig. 7c).⁵⁰,⁵¹ In parallel, photogenerated holes in the valence band of Cs₂AgBiBr₆ oxidize surface-bound water to O₂ and protons on the perovskite surface or on the RGO surface upon migration, possibly via Ag–O bonding.⁵² Protons then migrate across the interface at the DP–Cu–RGO heterostructure to Cu and the activated CO₂ to produce CH₄ (and minor CO) and H₂. Here Cu plays an important role facilitating the use of photoinduced electrons to activate CO₂ and form CH₄.⁵³,⁵⁴,⁵⁵ Along with the extended light absorption and CO₂ adsorption with the addition of Cu–RGO, the direct growth of Cs₂AgBiBr₆ on the Cu–RGO ensures a good interface and a large contact area, which improves charge separation to facilitate the challenging eight-electron reduction of CO₂ to CH₄.

Conclusions

We have successfully demonstrated a fast, surfactant/ligand-free and scalable mechanochemical synthesis of Cs₂AgBiBr₆ double perovskite (DP) nanoplates and their nanocomposites with Cu-decorated reduced graphene oxide (Cu–RGO). The resulting Cs₂AgBiBr₆–Cu–RGO nanocomposite shows significantly improved photocatalytic activity for CO₂ reduction to CH₄ (minor CO and H₂) using water vapor as proton and electron source, with 93.0 (±0.5)% CH₄ selectivity and an apparent quantum efficiency of 0.89 (±0.21)% in the absence of expensive hole scavengers such as alcohols but just simply water vapor. The optimum photocatalytic activity of 93 μmol e⁻ h⁻¹ g⁻¹ (at 1 sun) on total electron consumption basis is obtained for Cs₂AgBiBr₆–Cu–RGO, which is 13 times higher than Cs₂AgBiBr₆ double perovskite nanoplates. The activity increases to 122 μmol e⁻ h⁻¹ g⁻¹ at 2 suns. The high performance of the Cs₂AgBiBr₆–Cu–RGO nanocomposite for photocatalytic reductive CO₂ reflects the formation of an excellent interface between the Cs₂AgBiBr₆ and Cu–RGO, which promotes efficient photoinduced charge separation and lower recombination of electron–hole pairs. This is a result of electron transfer from the Cs₂AgBiBr₆ to Cu via RGO and simultaneous hole migration from Cs₂AgBiBr₆ to its surface or to the RGO, along with extended light absorption, larger surface area and improved CO₂ adsorption. In addition, improved reusability thanks to the hydrophobic character of RGO makes this Cs₂AgBiBr₆–Cu–RGO photocatalyst a potential Pb-free halide perovskite photocatalyst candidate for long-term application in solar fuel production. This strategy could be readily extended to prepare diverse Pb-free halide double perovskites for solar fuel applications.

Conflicts of interest

There are no conflicts to declare.

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