

Spin-Polarized Photocatalytic CO₂ Reduction of Mn-Doped Perovskite Nanoplates

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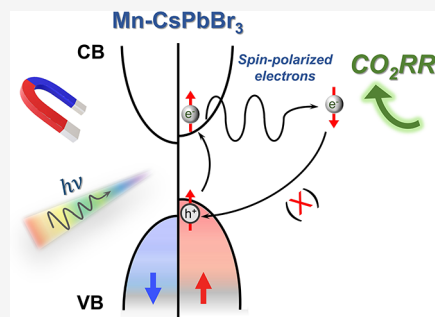


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Supporting Information

ABSTRACT: “Spin” has been recently reported as an important degree of electronic freedom to improve the performance of electrocatalysts and photocatalysts. This work demonstrates the manipulations of spin-polarized electrons in CsPbBr₃ halide perovskite nanoplates (NPLs) to boost the photocatalytic CO₂ reduction reaction (CO₂RR) efficiencies by doping manganese cations (Mn²⁺) and applying an external magnetic field. Mn-doped CsPbBr₃ (Mn-CsPbBr₃) NPLs exhibit an outstanding photocatalytic CO₂RR compared to pristine CsPbBr₃ NPLs due to creating spin-polarized electrons after Mn doping. Notably, the photocatalytic CO₂RR of Mn-CsPbBr₃ NPLs is significantly enhanced by applying an external magnetic field. Mn-CsPbBr₃ NPLs exhibit 5.7 times improved performance of photocatalytic CO₂RR under a magnetic field of 300 mT with a permanent magnet compared to pristine CsPbBr₃ NPLs. The corresponding mechanism is systematically investigated by magnetic circular dichroism spectroscopy, ultrafast transient absorption spectroscopy, and density functional theory simulation. The origin of enhanced photocatalytic CO₂RR efficiencies of Mn-CsPbBr₃ NPLs is due to the increased number of spin-polarized photoexcited carriers by synergistic doping of the magnetic elements and applying a magnetic field, resulting in prolonged carrier lifetime and suppressed charge recombination. Our result shows that manipulating spin-polarized electrons in photocatalytic semiconductors provides an effective strategy to boost photocatalytic CO₂RR efficiencies.



The origin of enhanced photocatalytic CO₂RR efficiencies of Mn-CsPbBr₃ NPLs is due to the increased number of spin-polarized photoexcited carriers by synergistic doping of the magnetic elements and applying a magnetic field, resulting in prolonged carrier lifetime and suppressed charge recombination. Our result shows that manipulating spin-polarized electrons in photocatalytic semiconductors provides an effective strategy to boost photocatalytic CO₂RR efficiencies.

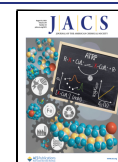
INTRODUCTION

Artificial photosynthesis using solar-driven CO₂ reduction to value-added fuels and chemicals has attracted great attention recently because it provides a promising strategy for simultaneously tackling two important environmental issues of global warming and renewable energy.^{1–4} However, because photocatalytic CO₂ reduction processes involve sluggish multielectron reaction kinetics, until now, the solar-driven CO₂ reduction conversion efficiency is still far from the satisfactory requirement for practical applications.^{5,6} Typically, the conversion efficiency of photocatalytic CO₂ reduction is governed by several determining factors such as light-harvesting, CO₂ adsorption, charge separation and transport of photogenerated carriers, and redox reaction.^{7,8} Extensive research has been devoted to pursuing efficient photocatalysts for CO₂ reduction by optimizing these key factors among materials.^{6,7,9} Halide perovskite semiconductors are an emerging class of solution-processable optoelectronic materials for high-performance solar cells and also for light-emitting diodes (LEDs) because they exhibit superior physical properties such as high optical absorption coefficients, low-cost fabrications, tunable band gaps, long diffusion lengths, and long carrier lifetime.^{10–14} Due to its excellent intrinsic

optoelectronic properties, halide perovskites have also recently demonstrated their great potential in photocatalyst applications of solar-driven CO₂ reduction or hydrogen evolution.^{15–21} Many efforts have been made to enhance the photocatalytic CO₂ reduction efficiencies and stabilities of halide perovskites.^{22–24} For example, it has been known that an effective strategy to enhance the photocatalytic CO₂ reduction efficiency is to construct heterojunctions of halide perovskites with other nanoscale materials to promote charge separation and suppress charge recombination.^{18,23,25,26} The creation of built-in electric fields at heterojunctions may significantly enhance the photoinduced carrier separation efficiencies and their corresponding photocatalytic CO₂ reduction performance.^{23,25,26}

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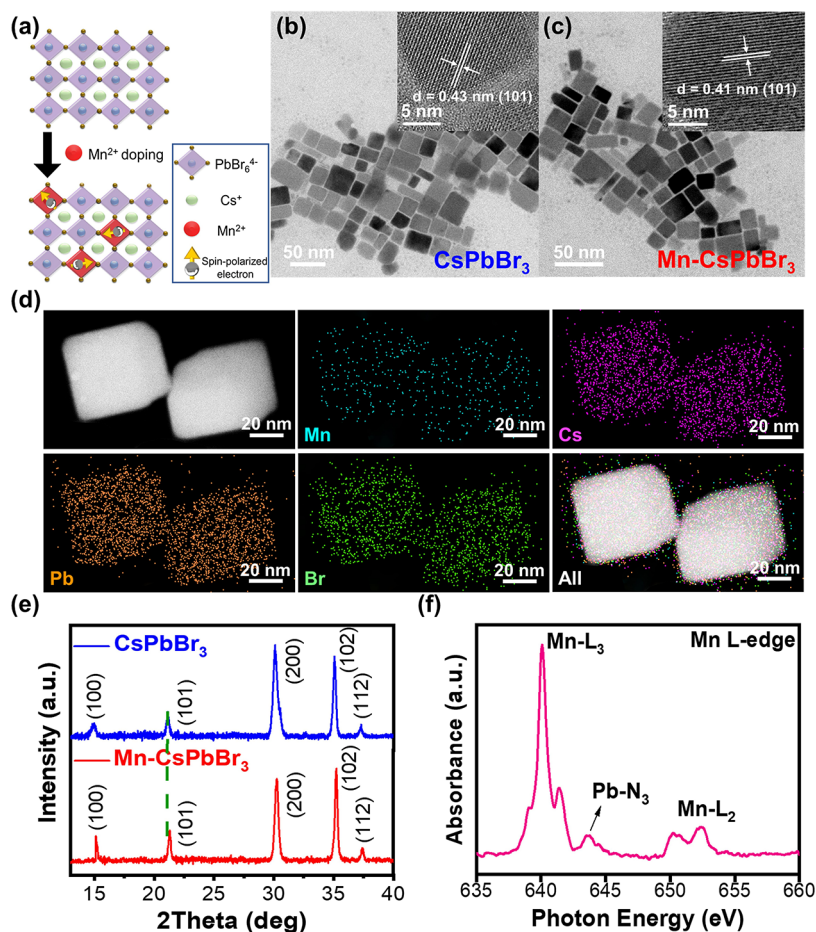


Figure 1. Morphology and structural characterization of CsPbBr₃ and Mn-CsPbBr₃ NPLs. (a) Schematic illustration of the formation of the electron spin polarization by doping magnetic Mn²⁺ ions in 3D all-inorganic perovskite CsPbBr₃. The TEM images of (b) CsPbBr₃ and (c) Mn-CsPbBr₃ NPLs. The insets are the HR-TEM images of CsPbBr₃ and Mn-CsPbBr₃ NPLs. (d) The HAADF-STEM and EDS element mapping (Mn, Cs, Pb, and Br) images of Mn-CsPbBr₃ NPLs. (e) The PXRD spectroscopy of CsPbBr₃ (blue) and Mn-CsPbBr₃ NPLs (red). (f) The Mn L_{3,2}-edge XANES spectroscopy of Mn-CsPbBr₃ NPLs.

“Spin”, which is the intrinsic characteristic property of electrons, has been recently reported as another important degree of electronic freedom to improve the performance of electrocatalysts and photocatalysts.^{4,27–31} Spin selection has been described as a possible way to promote electrocatalytic oxygen evolution reaction (OER), which involves the process of forming triplet-state O₂ from singlet-state species (OH⁻ or H₂O).^{32–34} Accordingly, the spin polarization of the active catalyst surface may favor the parallel spin alignment of oxygen atoms during the reaction.^{27,33} Inspired by the success of enhanced OER electrocatalytic activity by spin regulation, the manipulation of spin-polarized electrons is also an effective strategy to enhance the photocatalytic activities of materials.^{35–37} Because photocatalysis usually requires a rapid charge transfer and a prolonged lifetime of intermediate species for redox reactions, the spin polarizations of photoexcited electrons may play a positive role in the enhanced charge separation and suppression of charge recombination.^{35,36} For example, improved hydrogen evolution reaction (HER) and nitrogen reduction reaction (NRR) photocatalytic activities for metal oxides of TiO₂ and BaTiO₃ have been demonstrated recently.^{35,37} The generation of spin-polarized electrons by controlling the concentrations of metal or oxygen vacancies in these metal oxides may significantly enhance their photocatalytic activities.^{30,35–37} However, although creating vacan-

cies is an effective way to enhance spin-polarized electrons, the formation of traps and defects within the materials may simultaneously hinder the carrier diffusion and transport.³⁸ By contrast, doping magnetic elements into semiconductors could be another effective strategy to manipulate spin-polarized electrons in photocatalysis without largely sacrificing the crystallinity of the materials.^{39–41} Spin coupling of magnetic elements with semiconductors was shown to successfully modify their electronic, optical, and magnetic properties with the aim for spintronic applications.^{42–44}

In this work, we demonstrate that the photocatalytic CO₂ reduction conversion efficiencies can be significantly enhanced by manipulating the spin-polarized electrons of halide perovskite CsPbBr₃ nanoplates (NPLs). By doping with the magnetic element Mn, the photocatalytic CO₂ reduction efficiency of Mn-doped CsPbBr₃ (Mn-CsPbBr₃) NPLs can be significantly enhanced due to the increased spin polarization of photogenerated carriers and suppression of the charge recombination. Notably, the photocatalytic CO₂ reduction efficiencies of Mn-CsPbBr₃ NPLs can be further enhanced by applying an external magnetic field based on a permanent magnet. The Mn-CsPbBr₃ NPLs exhibit a 3.4 and 5.7 times improved performance of the photocatalytic CO₂ reduction reaction (CO₂RR) under a magnetic field of 100 and 300 mT, respectively, with a permanent magnet compared to the

pristine CsPbBr₃ NPLs. The origin of the enhanced photocatalytic CO₂ reduction efficiencies of Mn-CsPbBr₃ NPLs is mainly due to the prolonged carrier lifetime and suppressed charge recombination due to the enhanced spin-polarized photogenerated carriers. The mechanism is further systematically explored by magnetic circular dichroism (MCD) spectroscopy, ultrafast transient absorption (TA) spectroscopy, and density functional theory (DFT) simulations. Our result shows that manipulating spin-polarized electrons in semiconductors doped with magnetic elements provides an effective strategy to boost photocatalytic CO₂ reduction efficiencies.

RESULTS AND DISCUSSION

To obtain spin-polarized electrons in halide perovskite NPLs, the magnetic Mn²⁺ ions are designed to embed into the three-dimensional (3D) all-inorganic perovskite CsPbBr₃ NPLs, as shown in Figure 1a. These pristine CsPbBr₃ and Mn-CsPbBr₃ NPLs were synthesized via the traditional hot-injection method.^{45,46} The detailed synthesis method is described in the Supporting Information (SI). The structural morphology of both CsPbBr₃ and Mn-CsPbBr₃ NPLs is investigated by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HR-TEM), as shown in Figure 1b,c. The TEM morphological images in Figure 1b,c show that both CsPbBr₃ and Mn-CsPbBr₃ NPLs have a rectangular shape with an average size of around 45 nm. HR-TEM images corresponding to the (101) Miller plane of the 3D perovskite orthorhombic phase are shown in the inset of Figure 1b,c.⁴⁷ The observed interplanar spacing for the (101) plane of CsPbBr₃ and Mn-CsPbBr₃ NPLs was 0.43 and 0.41 nm, respectively. The thickness of both CsPbBr₃ and Mn-CsPbBr₃ NPLs was approximately 3 nm, as measured by atomic force microscopy (AFM) in Figure S1. Moreover, high-angle annular dark-field scanning transmission microscopy (HAADF-STEM) equipped with energy-dispersive X-ray spectroscopy (EDS) element mapping was applied to gain more insight into the incorporation of Mn²⁺ ion doping in Mn-CsPbBr₃ NPLs. Figure 1d shows the HAADF-STEM image of Mn-CsPbBr₃ NPLs and the corresponding EDS element mapping images of Cs, Pb, Br, and Mn. The Mn ions are homogeneously distributed among the Mn-CsPbBr₃ NPLs, as shown in the EDS mapping image of Mn (green dots). Furthermore, the quantitative Mn-doping ratio of Mn-CsPbBr₃ NPLs was approximately 3.2 mol %, as measured by inductively coupled plasma mass spectrometry (ICP-MS). The crystal structures of both CsPbBr₃ and Mn-CsPbBr₃ NPLs are measured by powder X-ray diffraction (PXRD) measurements, as shown in Figure 1e. The PXRD patterns of both CsPbBr₃ and Mn-CsPbBr₃ NPLs belong to the 3D perovskite orthorhombic phase, which echoes the aforementioned HR-TEM results and recent work.^{47,48} In particular, the PXRD patterns of Mn-CsPbBr₃ NPLs shift to a higher angle direction compared to the host CsPbBr₃ NPLs because of the substitution of the larger lead ion (ionic radius of Pb²⁺ is 1.33 Å) in the octahedral unit with the smaller manganese ion (ionic radius of Mn²⁺ is 0.97 Å) and the occupation of the interstitial sites, which result in lattice contraction.^{46,48,49} The observed shift in the angle is around 0.2°. The occupation of the interstitial sites can tailor the local crystal field, which is expected to tailor their radiation parameters and affect their anti-Stokes luminescence.⁴⁹ The valence and spin states of magnetic Mn ion doping into CsPbBr₃ NPLs were further

confirmed by Mn L_{3,2}-edge X-ray absorption near-edge structure (XANES) spectroscopy. Figure 1f shows that the normalized Mn L_{3,2}-edge XANES spectra of Mn-CsPbBr₃ matched the published MnO reference results, suggesting that the magnetic Mn ions in Mn-CsPbBr₃ NPLs are high-spin-state Mn²⁺ ions.^{50,51} These results indicate that the magnetic Mn²⁺ ions were successfully doped into the all-inorganic halide perovskite CsPbBr₃ NPLs.

Figure 2a,b shows the absorption and photoluminescence (PL) spectra of CsPbBr₃ and Mn-CsPbBr₃ NPLs. The absorption of CsPbBr₃ and Mn-CsPbBr₃ NPLs shows sharp excitonic absorption peaks at around 415 and 405 nm, respectively, which are clearly blue-shifted compared to the absorption peak of the conventional 3D CsPbBr₃ perovskite nanocube (500 nm).⁴⁵ Accordingly, the obvious blue shift of 85 and 95 nm in the absorption spectra for CsPbBr₃ NPLs and Mn-CsPbBr₃ NPLs, respectively, compared to the conventional 3D CsPbBr₃ perovskite nanocube originates from the quantum size effect due to the thin CsPbBr₃ and Mn-CsPbBr₃ NPLs (the thickness is about 3 nm from Figure S1).⁵² The corresponding PL spectra of CsPbBr₃ NPLs and Mn-CsPbBr₃ NPLs exhibited an excitonic emission peak position at 430 and 435 nm, respectively. Unlike CsPbBr₃ NPLs, an additional emission peak in the PL spectra is observed for Mn-CsPbBr₃ NPLs at around 600 nm due to the magnetic Mn²⁺ ions inducing a strong sp–d exchange interaction, which confirms the successful incorporation of Mn²⁺ into CsPbBr₃ NPLs.^{47,53} The incorporation of Mn²⁺ ion doping in CsPbBr₃ NPLs not only modifies their structural and optoelectronic properties but also induces spin polarization. Figure 2c shows the electron paramagnetic resonance (EPR) spectrum of Mn-CsPbBr₃ NPLs. The EPR spectrum of Mn-CsPbBr₃ NPLs exhibits a strong signal at approximately 3300 Gauss (corresponding to a g-factor of around 2) with six hyperfine splittings originating from the interaction between the magnetic Mn²⁺ ion nuclear spin ($S = 5/2$) and its electron spin.⁵⁴ By contrast, no EPR signal is observed for CsPbBr₃ NPLs. The feature of these broad six hyperfine splittings reveals that the magnetic Mn²⁺ ions also change the local structures of Mn-CsPbBr₃, resulting from a dipolar interaction.⁵⁵ Figure 2d shows the spin-polarized density of state (DOS) of Mn-CsPbBr₃ calculated by DFT simulation, where the difference in the DOSs of the spin-up and spin-down electrons around the Fermi level is calculated. The spin-polarized DOSs of both the valence band (VB) and conduction band (CB) of Mn-CsPbBr₃ originate from the doping magnetic Mn²⁺ ions. By contrast, no spin-polarized DOS is observed for the pristine CsPbBr₃ (Figure S3). The real-space charge distribution of the Mn-CsPbBr₃ is shown in the inset of Figure 2d, where a more localized character in proximity to the central Mn atom is observed. The result indicates that spin-polarized electrons are introduced by doping with the magnetic element Mn in the perovskite CsPbBr₃ NPLs.

Next, we examine the effect of enhanced spin-polarized electrons on the photocatalytic CO₂RR of CsPbBr₃ and Mn-CsPbBr₃ NPLs. The photocatalytic CO₂RR was demonstrated by placing CsPbBr₃ and Mn-CsPbBr₃ NPLs within CO₂-saturated water vapor under simulated solar irradiation AM 1.5G (100 mW cm⁻²), as shown in Figure S4. The detailed photocatalytic experiments are described in SI. Figure 2e shows that the main products of CsPbBr₃ and Mn-CsPbBr₃ NPLs for photocatalytic CO₂RR are CO and CH₄, respectively. The concentration of both CO and CH₄ increased

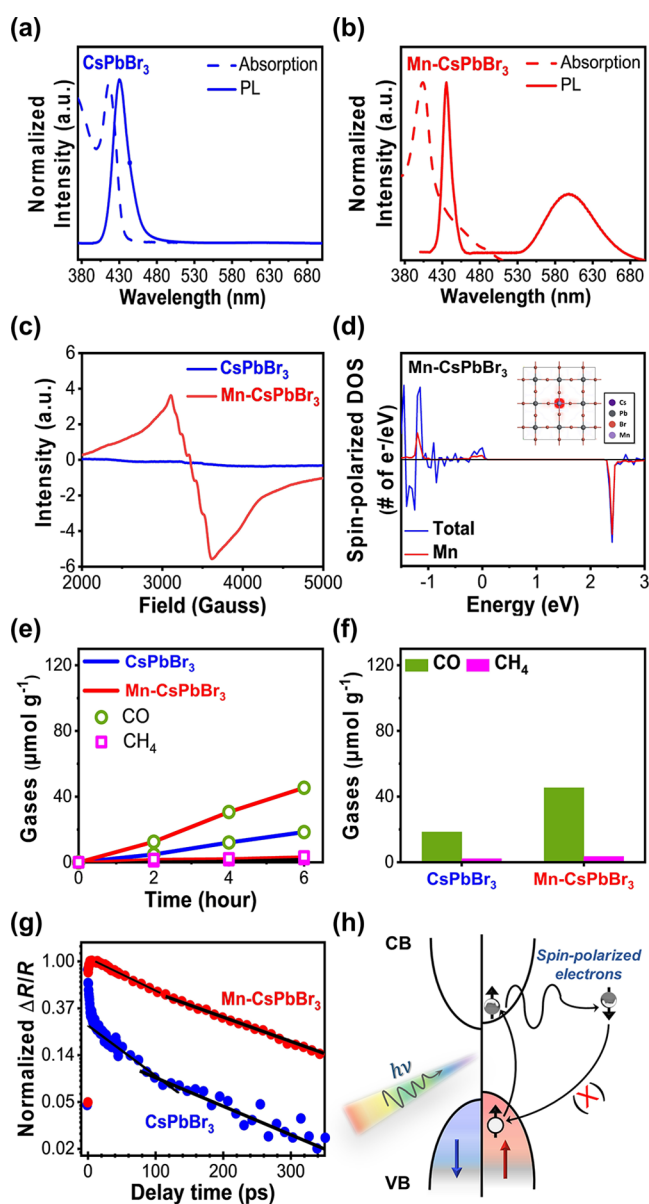


Figure 2. Optical properties, spin-polarized properties, and the photocatalytic performance of CsPbBr₃ and Mn-CsPbBr₃ NPLs. The UV–vis absorption and PL spectroscopy of (a) CsPbBr₃ and (b) Mn-CsPbBr₃ NPLs. (c) EPR spectroscopy of CsPbBr₃ (blue) and Mn-CsPbBr₃ (red) NPLs. (d) Spin-polarized DOS of Mn-CsPbBr₃ NPLs. The inset is the real-space charge distribution of Mn-CsPbBr₃ NPLs. (e) Product yields of CO and CH₄ gases over CsPbBr₃ and Mn-CsPbBr₃ NPLs during 6 h under AM 1.5 simulated solar irradiation. (f) The photocatalytic CO₂RR product yields of CsPbBr₃ and Mn-CsPbBr₃ NPLs after 6 h. (g) The normalized photoinduced transient reflectivity changes ($\Delta R/R$) of CsPbBr₃ and Mn-CsPbBr₃ NPLs. (h) Schematic illustration of the electron spin polarization suppressed the carrier recombination of Mn-CsPbBr₃ NPLs.

linearly during the 6 h (Figure S7). In addition, two control experiments (without light illumination and in a N₂ atmosphere) and ¹³CO₂ isotopic labeling experiments were performed. The results demonstrate that the products generated from photocatalytic CO₂RR over CsPbBr₃ NPLs originated from CO₂ rather than surface ligands, as shown in Figure S8. As shown in Figure 2f, the product yields of CO and CH₄ over the pristine CsPbBr₃ NPLs are 18.4 and 2.1 $\mu\text{mol g}^{-1}$, respectively, which are comparable with the reported

product yields of CsPbBr₃ nanocrystals,^{18,22,24,56–58} as shown in Table S1. By contrast, the corresponding product yields of CO and CH₄ over Mn-CsPbBr₃ NPLs are 45.4 and 3.5 $\mu\text{mol g}^{-1}$, respectively, which are remarkably higher than the product yields over the pristine CsPbBr₃ NPLs. The Mn-CsPbBr₃ NPLs exhibit a higher photocatalytic activity for the CO₂ reduction reaction compared to the pristine CsPbBr₃ NPLs, mainly resulting from the presence of spin-polarized electrons induced by the doping of magnetic Mn²⁺ ions. To further investigate the corresponding carrier dynamics of CsPbBr₃ and Mn-CsPbBr₃ NPLs, we applied an ultrafast pump–probe measurement. As shown in Figure 2g, the photoinduced transient reflectivity changes ($\Delta R/R$) reveal that the photoexcited electrons in the CB release their energy through the intraband electron–electron scattering and the excitons decay via the phonon-assisted nonradiative recombination.⁵⁹ As a result, a prolonged nonradiative recombination lifetime can be observed for the Mn-CsPbBr₃ NPLs (τ_1 : 54.5 ps and τ_2 : 261.5 ps) compared to the pristine CsPbBr₃ NPLs (τ_1 : 10.9 ps and τ_2 : 135.9 ps; more details in the SI) because of the suppression of the carrier recombination rate due to the presence of spin polarization electrons. The experimental observation can be further explained by the mechanism of quantum spin exchange interactions (QSEIs), as reported in studies.^{60–63} QSEI can stabilize open-shell orbital configurations with unpaired electrons in magnetic compositions, which are important in catalysts with configurations consisting of unpaired electrons. Doping of high-spin magnetic Mn²⁺ ions (with 3d orbitals) in the perovskite semiconductors leads to the presence of spin-polarized electrons and nonsymmetric DOS, as shown in Figure 2h. By contrast, the pristine CsPbBr₃ NPLs with symmetric DOS lack spin-polarized electrons, as seen in Figure S3. After light illumination, the spin-polarized electrons of Mn-CsPbBr₃ NPLs are excited to the CB, while the spin-polarized holes with the same spin direction remain in the valence band (VB). The presence of QSEI increases the exchange of electron spin delocalization and decreases the repulsion of the electrons, leading to the spin-correlated unpaired electrons being more stable at the energy states.⁶⁰ Therefore, the QSEI can efficiently make the electrons with the same spin direction to transport easily.⁶⁰ Meanwhile, the photoexcited spin-polarized electrons in the CB are likely to undergo spin relaxation (or spin-flip) and lose their original spin direction during the charge-transfer process due to the strong spin–orbital coupling and hyperfine interaction.^{35,36} The strong spin–orbital coupling of Mn-CsPbBr₃ NPLs mainly originated from the quantum confinement effect and heavy Pb²⁺ atoms.^{44,64} Accordingly, the carrier recombination rate is largely suppressed because of the lack of spin-polarized holes with the same spin direction in the VB. This may lead to a longer carrier lifetime of Mn-doped CsPbBr₃ compared to that of the pristine CsPbBr₃. On the other hand, the doping of high-spin magnetic Mn²⁺ ions in CsPbBr₃ can also affect the photocatalytic oxygen evolution reaction (OER) due to the presence of QSEI.^{60,62,63} The QSEI can help to stabilize the antibonding 3d orbitals and accumulate the spin-polarized holes for bonding with oxygen molecules, leading to enhanced photocatalytic OER activity as compared to the pristine CsPbBr₃.⁶² Therefore, the presence of spin-polarized electrons induced by the doping of magnetic Mn²⁺ ions in CsPbBr₃ NPLs may effectively facilitate the redox reactions for the photocatalytic CO₂RR compared to the pristine CsPbBr₃ NPLs.

Moreover, it is well known that the electron spin polarization in semiconductors can be further enhanced by applying an external magnetic field.^{35,36,65,66} Here, an external magnetic field of up to 300 mT is applied to further enhance the photocatalytic performance of Mn-CsPbBr₃ NPLs. A permanent magnet that requires no extra power supply is used as the source of the external magnetic field. The experimental setup of the photocatalytic CO₂RR with permanent magnets is shown in Figures S4 and S5. Figure 3a,b shows the evolution of

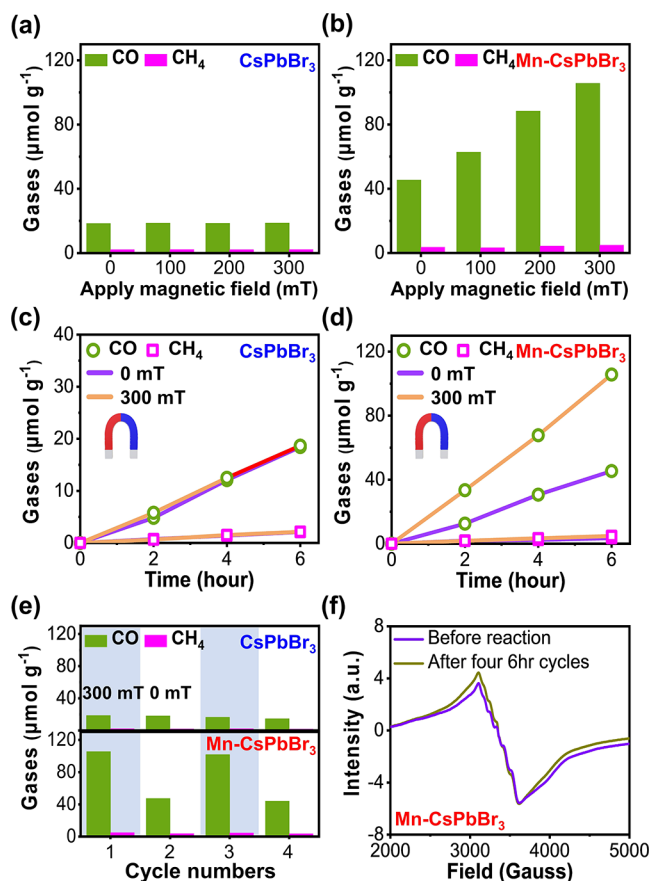


Figure 3. Photocatalytic performance of CsPbBr₃ and Mn-CsPbBr₃ NPLs with and without an external magnetic field. The photocatalytic CO₂RR product yields of (a) CsPbBr₃ and (b) Mn-CsPbBr₃ NPLs under different external magnetic fields (from 0 to 300 mT) after 6 h of light illumination. Product yields of CO and CH₄ gases over (c) CsPbBr₃ and (d) Mn-CsPbBr₃ NPLs with and without an external magnetic field (0 and 300 mT) during 6 h under light irradiation. (e) The photocatalytic stability test of CsPbBr₃ (up) and Mn-CsPbBr₃ (down) NPLs with and without an external magnetic field (0 and 300 mT) for four 6 h cycles. (f) EPR spectroscopy of Mn-CsPbBr₃ NPLs before and after four 6 h cycles of the photocatalytic CO₂RR.

the photocatalytic CO₂RR of pristine CsPbBr₃ and Mn-CsPbBr₃ NPLs under an external magnetic field ranging from 0 to 300 mT. For the pristine CsPbBr₃ NPLs, the product yields of both CO and CH₄ are unaltered with the increase of the external magnetic field from 0 to 300 mT. By contrast, the enhancement of the photocatalytic performance over Mn-CsPbBr₃ NPLs highly correlates with the increase of the external magnetic field from 0 to 300 mT. The evolution of the product yields of both CO and CH₄ for the pristine CsPbBr₃ NPLs and Mn-CsPbBr₃ NPLs with and without a magnetic

field is shown in Figure 3c,d, respectively. The product yield of CO over Mn-CsPbBr₃ NPLs under 300 mT (105.7 μmol g⁻¹) is 2.3 times larger than that under 0 mT (45.4 μmol g⁻¹), while the product yield of CH₄ under 300 mT (4.8 μmol g⁻¹) is 1.6 times larger than that under 0 mT (3.5 μmol g⁻¹), as shown in Figure 3d. The results indicate that the photocatalytic CO₂RR performance of Mn-CsPbBr₃ NPLs can be further enhanced by applying an external magnetic field. By contrast, no such correlation is found over the pristine CsPbBr₃ NPLs. Figure 3e shows the superior photocatalytic stability and reproducibility of Mn-CsPbBr₃ NPLs with the product yields of both CO and CH₄ after four consecutive cycles with and without an external magnetic field (0 and 300 mT). Figure 3f also shows that the EPR signature of the spin-polarized properties of Mn-CsPbBr₃ NPLs is almost unchanged after four 6 h cycles. The result suggests that the excellent stability of the photocatalytic performance of Mn-CsPbBr₃ NPLs can be achieved by applying an external magnetic field over 24 h.

The above results indicate that the photocatalytic CO₂RR efficiencies of Mn-CsPbBr₃ NPLs greatly correlate with the electron spin polarization. We performed MCD spectroscopy and ultrafast TA spectroscopy under a magnetic field to further examine the origin of the magnetic field-enhanced photocatalytic CO₂RR over Mn-CsPbBr₃ NPLs. MCD is the difference in absorption between the left circular polarized (A_{LCP}) and right circular polarized (A_{RCP}) lights as the linearly polarized light is transmitted to a medium under a magnetic field, originating from the splitting of states by the Zeeman splitting energy ΔE_z . The presence of the MCD signal indicates the existence of a spin-polarized band structure. Figure 4a,b shows the MCD spectra of pristine CsPbBr₃ and

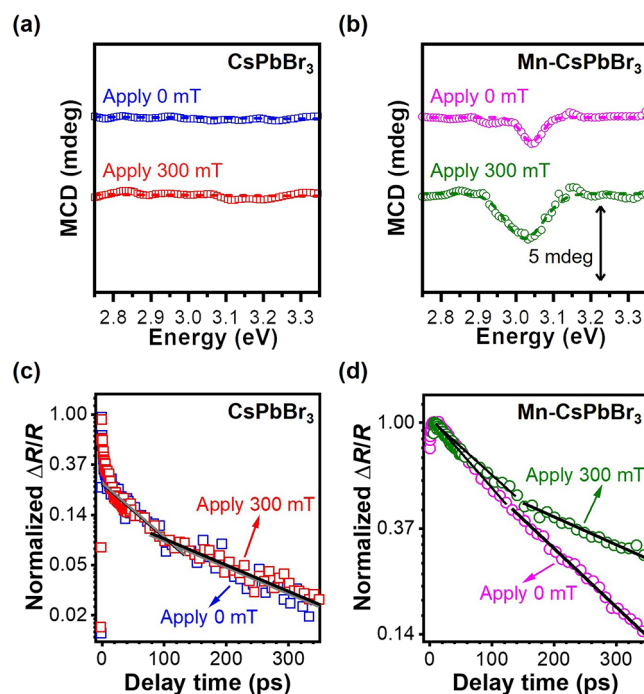


Figure 4. MCD spectroscopy and ultrafast carrier dynamics of CsPbBr₃ and Mn-CsPbBr₃ NPLs with and without an external magnetic field. The MCD spectroscopy of (a) CsPbBr₃ and (b) Mn-CsPbBr₃ NPLs with and without an external magnetic field (0 and 300 mT). The normalized photoinduced transient reflectivity changes ($\Delta R/R$) of (c) CsPbBr₃ and (d) Mn-CsPbBr₃ NPLs with and without an external magnetic field (0 and 300 mT).

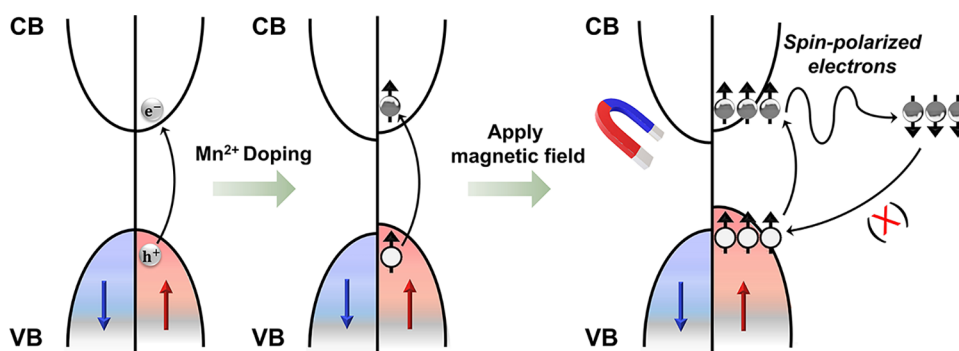


Figure 5. Schematic illustration of the electron spin polarization induced a longer photoexcited carrier lifetime under an external magnetic field in Mn-CsPbBr₃ NPLs.

Mn-CsPbBr₃ NPLs under 0 and 300 mT, respectively. No detectable MCD signal is observed for the pristine CsPbBr₃ with and without a magnetic field. By contrast, the presence of an MCD signal at the Mn-CsPbBr₃ NPLs without a magnetic field (0 mT) indicates an intrinsic spin-polarized band structure. Because the energy position of the MCD peak is close to the energy gap of the Mn-CsPbBr₃ NPLs, the origin of the MCD signal is attributed to the intrinsic spin-polarized band splitting near the band edges due to the doping of magnetic Mn²⁺ ions. When a magnetic field was applied, the magnitude of the band splitting in Mn-CsPbBr₃ NPLs is increased due to the Zeeman effect, leading to an enhanced MCD signal. The result indicates that the spin polarization of the photoexcited carriers of Mn-CsPbBr₃ NPLs can be significantly enhanced under an external magnetic field. The corresponding carrier dynamics of CsPbBr₃ and Mn-CsPbBr₃ NPLs with and without an external magnetic field were further verified by the ultrafast pump–probe measurement under an external magnetic field. Figure 4c,d shows the transient reflectivity changes $\Delta R/R$ decay curves of CsPbBr₃ and Mn-CsPbBr₃ NPLs with and without an external magnetic field, respectively. Mn-CsPbBr₃ NPLs exhibit both biexciton (τ_1) and single exciton (τ_2) decays with a prolonged relaxation lifetime from $\tau_1 = 54.5$ ps and $\tau_2 = 261.5$ ps (0 mT) to $\tau_1 = 93.0$ ps and $\tau_2 = 369.5$ ps (300 mT), respectively, as a result of the suppressed phonon-assisted nonradiative recombination rates. By contrast, there is no change in the transient reflectivity changes $\Delta R/R$ decay curves of pristine CsPbBr₃ NPLs with and without an external magnetic field. The enhanced electron spin polarization of Mn-CsPbBr₃ NPLs under an external magnetic field results in a prolonged lifetime of the photogenerated charge carriers, which significantly reduces the carrier recombination. This may enhance the diffusion of the photogenerated carriers to the surface to facilitate the redox reactions for the photocatalytic CO₂RR. Figure 5 summarizes the correlation between manipulating the spin polarization of Mn-CsPbBr₃ NPLs and enhancing the photocatalytic CO₂RR. First, the spin-polarized bands in both the VB and CB are obtained by doping the magnetic Mn²⁺ ions into the perovskite CsPbBr₃ NPLs. Under light illumination, the spin-polarized electrons in Mn-CsPbBr₃ NPLs result in a longer carrier lifetime and a slower recombination rate compared to those in the pristine CsPbBr₃ NPLs. Meanwhile, the enhanced spin-polarized holes in VB may also facilitate the oxidation reaction process. This explains the enhanced performance of the photocatalytic CO₂RR in Mn-CsPbBr₃ NPLs compared to that in the pristine CsPbBr₃ NPLs. After an

external magnetic field is applied, the enhanced splitting of the spin-polarized bands in Mn-CsPbBr₃ NPLs due to the Zeeman effect leads to the further increase of spin-polarized electrons and holes. This may further suppress the carrier recombination rate and facilitate the overall redox reactions for the photocatalytic CO₂RR, contributing to the improved photocatalytic performance. The above mechanism indicates that manipulating the spin polarization in Mn-CsPbBr₃ NPLs by doping magnetic Mn²⁺ ions or applying a magnetic field is an effective strategy to boost the photocatalytic CO₂ reduction efficiencies.

CONCLUSIONS

In summary, we designed and synthesized spin-polarized halide perovskite NPLs via doping magnetic Mn²⁺ ions in all-inorganic CsPbBr₃ perovskite NPLs. With synergistic doping of the magnetic elements and applying a magnetic field, the photocatalytic CO₂ reduction efficiencies of Mn-CsPbBr₃ NPLs are largely improved compared to those of the pristine CsPbBr₃ NPLs. It results from the significantly suppressed carrier recombination rates due to the enhanced spin polarization of Mn-CsPbBr₃ NPLs. It is worth noting that such considerably enhanced photocatalytic CO₂ reduction efficiencies of Mn-CsPbBr₃ NPLs can be achieved by simply applying a permanent magnet without additional power consumption, which works as a promising and feasible approach as considering in the future application of solar to fuel conversion.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.2c06060>.

Experimental section, AFM data, band gaps of perovskite NPLs, spin-polarized DOS of the pristine CsPbBr₃, setup of photocatalytic CO₂RR, calibration curves of CO and CH₄, evolutions of products over perovskite NPLs under different external magnetic fields, control experiments and ¹³CO₂ isotopic experiment, comparison of photocatalytic CO₂RR conversion efficiencies, decay times of perovskite NPLs, and setup of MCD measurements (PDF)

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