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BoostingPhotocatalyticCO2ReductiononCsPbBr3PerovskiteNanocrystalsbyImmobilizing Metal Complexes

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ABSTRACT: Converting CO_2 into chemical fuels with a photocatalyst and sunlight is an appealing approach to address climate deterioration and energy crisis. Metal complexes are superb candidates for CO₂ reduction due to their tunable catalytic sites with high activity. The coupling of metal complexes with organic photosensitizers is regarded as a common strategy for establishing photocatalytic systems for visible-light-driven CO₂ reduction. While most of the organic photosensitizers generally contain precious metals and are available through onerous synthetic routes, their large-scale application in the photocatalysis is limited. Halide perovskite nanocrystals (NCs), have been considered as one of the most promising light-harvesting materials to replace the organic photosensitizers due to their tunable light absorption range, low cost, abundant surface sites, high molar extinction coefficient. Herein, we demonstrate a facile strategy to immobilize $[Ni(terpy)_2]^{2+}$ (Ni(tpy)) on inorganic ligand-capped CsPbBr₃ NCs and to apply this hybrid as catalyst for visible light-driven CO₂ reduction. In this hybrid photocatalytic system, the Ni(tpy) can provide specific catalytic sites and serve as electron sinks to suppress electron-hole recombination in the CsPbBr₃ NCs. The CsPbBr₃-Ni(tpy) catalytic system achieves a high yield (1724 μ mol/g) in the reduction of CO₂ to CO/CH₄, which is approximately 26-fold higher than that achieved with the pristine CsPbBr₃ NCs. This work has developed a method for enhancing the performance of photocatalytic CO₂ reduction by immobilizing metal complexes on perovskite NCs. The methodology we present here provides a new platform for utilizing halide perovskite NCs for photocatalytic applications.

INTRODUCTION

Photocatalytic CO₂ reduction offers a potential solution to simultaneously address the problems of the depletion of fossil fuels and global warming.^(1,2) Although significant advances have been reported,⁽³⁻⁸⁾ the development of robust, selective, and inexpensive visible-light-driven photocatalysts for CO₂ reduction remains crucial. In recent years, metal complexes have been widely used for photocatalysis.⁽⁹⁻¹²⁾ These metal complexes often have multi- π electron conjugated structures, which contribute to their electron transfer and storage abilities.^(13,14) Moreover, the catalytic activity of metal complexes can be easily tailored by altering the central metal ions or the surrounding ligands.⁽¹⁵⁾ These attractive properties make them superb candidates for multielectron-transfer catalysis in CO2 reduction. However, most metal complexes have limited visible-light response, which is an obstacle to their use in visible-lightdriven CO₂ reduction. A common strategy for broadening its visible-light absorption range is to metal complexes with organic photosensitizers, such as fac-tris(2couple these phenylpyridine)iridium (Ir(ppy)₃), tris(bipyridine)ruthenium(II) chloride (Ru(bpy)₃), or organic dve.⁽¹⁶⁻¹⁸⁾ These sensitizers, however, either contain precious metals or suffer the problem of onerous synthetic routes, which limits their large-scale application.

Compared to organic photosensitizers, semiconductor nanocrystal (NCs) generally have a higher molar extinction coefficient and exhibit a broader visible-light absorption range.⁽¹⁹⁾ Furthermore, these NCs have the advantages of convenient synthesis, tunable light absorption range, low cost, and abundant surface sites.^(2,7,20-22) Therefore, colloidal NCs are potentially ideal candidates to replace organic photosensitizers. Among others, halide perovskite NCs have been found to be great alternatives to well-established chalcogenide NCs.⁽²³⁾ In addition to the advantages mentioned above, the perovskite NCs also have relatively low nonradiative

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recombination rates, tunable chemical composition and structure via post-synthetic transformations.⁽²⁴⁾ Furthermore, perovskite NCs have also proven to be one of the most promising materials for designing highly efficient photocatalytic systems.⁽²⁵⁻⁴⁰⁾

Therefore, the coupling of perovskite NCs with metal complexes is expected to solve the problems caused by the use of organic photosensitizers and form more efficient photocatalytic systems. In this context, the visible-light absorption range of metal complexes can be expanded by coupling with perovskite NCs; meanwhile these metal complexes are likely to provide catalytic sites for perovskite NCs and capture photoexcited electrons from perovskite NCs for selective photocatalytic reduction of CO₂. Furthermore, coupling metal complexes with perovskite NCs has the following advantages: 1) the abundant binding sites on perovskite NCs can be readily modified for immobilizing metal complexes; 2) the immobilized metal complexes can provide catalytic sites for perovskite NCs, and these specific catalytic sites are expected to enhance the catalytic performance of the CO_2 reduction; 3) the metal complexes can serve as the electron sinks which are able to accept multiple photoexcited electrons from the perovskite NCs in a stepwise manner. This is particularly important for multielectron reductions of CO₂, which can proceed at relatively low potentials.⁽⁴¹⁾ In other words, this architecture can combine the advantages of homogeneous (e.g., metal complexes) and heterogeneous (e.g., perovskite NCs) catalysis and potentially provides an efficient system for CO₂ reduction.

In this work, we present a novel hybrid photocatalyst system based on immobilizing transition metal complexes onto modified CsPbBr₃ perovskite NCs for visible-light-driven CO₂ reduction. As a proof of concept, Ni(tpy) (nickel complex with 2,2':6',2''-terpyridine, $[Ni(terpy)_2]^{2+}$) was selected as the metal complex. One of the reason for choosing Ni(tpy) is that it does not contain noble metal and it has polypyridyl rings for capturing and storing electrons.⁽⁴²⁻

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⁴³⁾ In this system (CsPbBr₃-Ni(tpy)), the catalytic efficiency of the CsPbBr₃ NCs was found to be dramatically improved by the immobilizing of Ni(tpy). The photocatalytic activity of CsPbBr₃-Ni(tpy) for CO₂ reduction is 26-fold higher than that of pristine CsPbBr₃ NCs. Further investigations revealed the electron transfer kinetics between the CsPbBr₃ NCs and Ni(tpy) through time-resolved fluorescence decay (TRPL) and transient absorption (TA) spectra. We demonstrated that the coupling of metal complexes is a promising strategy to improve the photocatalytic properties of perovskite NCs. This strategy also provides a platform for designing precious-metal-free photocatalysts for CO₂ reduction.

EXPERIMENTAL SECTION

Chemicals. Cs₂CO₃ (99.9%), octadecene (ODE, 90%), oleic acid (OA, 90%), PbBr₂ (98%), ethyl acetate (EA, 99.8%, Anhydrous), acetonitrile (ACN, 99.8%, Anhydrous), ferrocene (98%) were purchased from Sigma-Aldrich. Oleylamine (OAm, 80-90%) and 2,2':6',2"-terpyridine (terpy, 97%) were purchased from Alfa Aesar. Ammonium hexafluorophosphate (NH₄PF₆, 95%), NiCl₂·6H₂O (99.9%), hexane, ethanol, ether, acetone, toluene and tetrabutylammonium hexafluorophosphate (TBAPF₆, 98%) were purchased from Aladdin. All chemicals were used as received without any further purification. ¹³CO₂ (>99 atom% ¹³C) was purchased from Sigma Aldrich.

Preparation of the Cs-OA Precursor. Cs_2CO_3 (100 mg), OA (0.6 mL), and ODE (4 mL) were loaded into a 50 mL three-neck round-bottom flask. The reaction system vacuumed at 100 °C for 1h, and then heated under N₂ flow to 150 °C until all the Cs_2CO_3 are dissolved in ODE. The temperature of the Cs-Oleate precursor was cooled down to 100 °C and maintaining at this temperature before injection.

Synthesis of pristine CsPbBr₃ NCs. The organic ligands (OL) capped CsPbBr₃ NCs were prepared according to a literature procedure.⁽⁴⁴⁾ Briefly, ODE (5 mL) and PbBr₂ (0.188 mmol) were loaded into 50 mL 3-neck round-bottom flask and dried under vacuum at 120 °C for 1h. Subsequently, dried OAm (0.5 mL) and dried OA (0.5 mL) were injected at 140 °C under N₂. After complete dissolution of a PbBr₂ salt, the temperature was raised to 180 °C and Cs-oleate solution (0.5 mL, 0.125 M) was quickly injected and, 5 s later, the reaction mixture was cooled by the ice-water bath. The crude NCs solution was dispersed in 5 mL hexane, and the undissolved particles were separated by centrifuging the solution at 6000 rpm for 5 min. The supernatant was collected and the pristine CsPbBr₃ particles were precipitated by adding EA (hexane: EA = 1:1, v:v), and the aggregation was separated by centrifuging the solution at 6000 rpm for a form.

Preparation of PF₆ modified CsPbBr₃ NCs (PF₆-CsPbBr₃). Ligand exchange was performed under dark condition by a modified literature procedure.⁽⁴⁵⁾ Briefly, the pristine CsPbBr₃ (5 mg) was re-dispersed in EA (5 mL, solution A). An ethanol solution of NH₄PF₆ (40 μ L, 20 mM) was added into solution A and stirred in the dark for 30 min to form PF₆⁻ modified CsPbBr₃ NCs. The stripped particles were centrifuged (5000 rpm, 5 min) and dried in air. Similar procedures were employed for the preparation of EA treated CsPbBr₃ NCs except the absence of NH₄PF₆.

Assembly of CsPbBr₃-Ni(tpy). In a typical process, the PF₆-CsPbBr₃ NCs were redispersed in EA (5 mL, solution B). An acetonitrile solution of Ni(tpy) (40 μ L, 6 mM) (detailed chemical structure was shown in Figure S1) was added into solution B and stirred in the dark for 10 min to form CsPbBr₃-Ni(tpy) composites. The CsPbBr₃-Ni(tpy) composites were separated by centrifuging the resulted solution at 5000 rpm for 5 min. After centrifugation, the supernatant was discarded and the CsPbBr₃-Ni(tpy) catalysts were dried for further characterizations and applications.





Figure 1. (a) Schematic of the formation of CsPbBr₃-Ni(tpy) photocatalysts. (b) Fourier transform infrared (FT-IR) spectra of the pristine CsPbBr₃ (black), PF₆-CsPbBr₃ (dark green) and

CsPbBr₃-Ni(tpy) (dark red). (c) Variations in the zeta (ζ) potentials of the pristine CsPbBr₃, PF₆-CsPbBr₃ and CsPbBr₃-Ni(tpy) in EA.

High-quality colloidal CsPbBr₃ NCs were synthesized using a typical hot injection method developed by Protesescu et al. (see experimental for details).⁽⁴⁴⁾ The pristine CsPbBr₃ NCs are usually capped by long aliphatic chain-containing organic ligands such as OA and OAm.⁽⁴⁶⁾ The presence of these bulky ligands forms a barrier on the surface of the NCs, thereby hindering the assembly of CsPbBr₃-Ni(tpy). At the same time, these ligands also inhibit the adsorption of potential substrates (e.g., CO_2) and reduce the catalytic activity of NCs. Therefore, in order to maximize the coupling of NCs to Ni(tpy) and/or to CO_2 , it is necessary to remove or replace the OLs. To this end, we propose a novel strategy to assemble CsPbBr₃-Ni(tpy) catalysts. As depicted in Figure 1a, first, the EA can help to remove the native organic molecules capped on the CsPbBr₃ NCs (Figure S2), upon the ligand removal, the NCs display a more positively charged surface enabling a higher amount of PF₆⁻ to immobilize on the CsPbBr₃ NCs via electrostatic interactions. Replacing native OL with PF_6^- can significantly reduce the steric hindrance of the NC surface. At the same time, the surface charge of the NCs may be altered by the negatively charged PF_6 . Subsequently, Ni(tpy) was introduced into the PF_6 -CsPbBr₃ NCs. Due to the strong electrostatic interaction between PF_6^- and Ni(tpy) on NCs, Ni(tpy) was immobilized on CsPbBr₃ to form a CsPbBr₃-Ni(tpy) catalyst (details of the CsPbBr₃-Ni(tpy) assembly process are presented in the Experimental Section).

To monitor the assembly process, we examined the ligand species present on the NC samples using FT-IR spectroscopy. As shown in Figure 1b, for the pristine CsPbBr₃, three typical bands for hydrocarbon species appear at 2852, 2925 and 1466 cm⁻¹, indicating the presence of long-chain organic ligands.⁽⁴⁷⁾ Additionally, four bands assigned to C=O, COO⁻, N-

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H and N-H vibrations appear at 1710, 1394, 1633 and 3420 cm⁻¹, respectively, which indicate the coexistence of OAm and OA on the surface of the pristine CsPbBr₃ NCs.⁽⁴⁸⁾ At the same time, for the PF₆-CsPbBr₃, the intensities of the OA- and OAm-related peaks significantly decrease, revealing the desorption of OA and OAm from the NC surface. In addition, the appearance of the characteristic band of PF_6^- at 835 cm⁻¹ confirmed the adsorption of PF_6^- on the NC surface (see Figure S3 for the characteristic bands of NH₄PF₆). Compared with the PF₆-CsPbBr₃, the CsPbBr₃-Ni(tpy) shows new bands from 800 to 1600 cm⁻¹ (Figure 1b) being characteristic for Ni(tpy)-containing species (see Figure S3 for the FTIR spectrum of Ni(tpy)). The FT-IR also indicated that the Ni(tpy) were adsorbed on the surface of CsPbBr₃ rather than physically mixed with CsPbBr₃. Compared with the Ni(tpy) or the CsPbBr₃, there is no any shifts in the peaks for the CsPbBr₃-Ni(tpy). The FT-IR spectrum of CsPbBr₃-Ni(tpy) is a superposition of Ni(tpy) and CsPbBr₃ NC signals revealing the Ni(tpy) are immobilized to the NC surface by electrostatic interactions rather than by chemical bonding. In addition, with the adsorption of the $[Ni(terpy)_2]^{2+}$, some of the free PF₆⁻ (from Ni(tpy)) will be further adsorbed onto the NC surface, leading to a higher peak intensity at 835 cm⁻¹ in the CsPbBr₃-Ni(tpy).

To investigate the mechanism of the CsPbBr₃-Ni(tpy) assembly, we measured the zeta (ζ) potentials of various NC samples. As is seen from Figure 1c, the pristine CsPbBr₃ NCs carry a positive charge on their surfaces (ζ potential of +5.8 mV). After ligand exchange with PF₆⁻, the surface of the CsPbBr₃ became negatively charged facilitating further introduction of positively charged Ni(tpy). These results demonstrated that the OL on the CsPbBr₃ NCs could be replaced by PF₆⁻, allowing the immobilizing of Ni(tpy) on the CsPbBr₃ NCs *via* electrostatic interactions. The X-ray diffraction (XRD) patterns (Figure S4) indicated that the NCs were highly crystalline,



a

and their cubic perovskite crystal phase was well maintained during the formation of CsPbBr₃-Ni(tpy).

b

CsPbBr₃-Ni(tpy)

Ni 2p



Figure 2. (a-b) UV-vis absorption spectra and X-ray photoelectron spectra (XPS) of CsPbBr₃ and CsPbBr₃-Ni(tpy), respectively. (c-d) Transmission electron microscopy (TEM) images of CsPbBr₃ and CsPbBr₃-Ni(tpy), the insets show the high resolution TEM (HRTEM) images of the corresponding samples.

To confirm the Ni(tpy) was successfully immobilized on the CsPbBr₃ surface, we analyzed the NC samples by UV-vis absorbance and X-ray photoelectron spectroscopy (XPS). Figure 2a

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shows that the pristine CsPbBr₃ NCs and CsPbBr₃-Ni(tpy) display similar profiles in the visible spectral region with absorption maxima around 508 nm. In addition, the spectrum of CsPbBr₃-Ni(tpy) showed apparent characteristic absorption peaks below 400 nm, confirming the presence of Ni(tpy) on the NC surface. It is also evidenced that the Ni(tpy) alone could not absorb visible light, we can infer that under visible-light irradiation, Ni(tpy) acts as the catalyst and CsPbBr₃ plays the role of the photosensitizer in the CsPbBr₃-Ni(tpy) hybrid system. It should be noted that the absorption tail for CsPbBr₃-Ni(tpy) is extended to ~ 600 nm (Figure 2a). One of the possible reasons may be a stronger coupling between NCs caused by the ligand exchange.⁽⁴⁹⁾ The assembly of CsPbBr₃-Ni(tpy) was further confirmed by the XPS spectra shown in Figure 2b. To the signals of the characteristic elements (Cs, Pb and Br), we observed two peaks from Ni 2p in the CsPbBr₃-Ni(tpy). Furthermore, in the high resolution XPS shown in Figure S5, we observed the shift of binding energies in Cs, Pb, Br and N. These outcomes are principally due to the strong chemical interactions at the interface between the CsPbBr₃ and the tpy, leading to the redistribution of charges in CsPbBr₃-Ni(tpy). The TEM images in Figure 2c-2d show that the pristine CsPbBr₃ NCs are highly crystalline nanocubic, and the particle size of the CsPbBr₃ NCs remained constant (ca. 9.8 nm) during ligand exchange and catalyst immobilization. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energydispersive X-ray spectroscopy (EDS) elemental mapping shown in Figure S6 further confirm that the five representative elements (i.e., Cs, Pb, Br, Ni and F) are uniformly distributed throughout the sample indicating the presence of PF_6^- and Ni(tpy) on the surface of CsPbBr₃-Ni(tpy) NCs.



Figure 3. (a) Tauc plot of $(\alpha hv)^2 vs hv$ based on the UV-vis absorption spectra of CsPbBr₃ (the mentioned CsPbBr₃ hereafter refer to the PF₆ modified CsPbBr₃ NCs unless otherwise stated). (b) XPS spectra of CsPbBr₃: the valence band edge region. From these data, we could estimate that the valence band (VB) position of CsPbBr₃ NCs was -5.98 V *vs.* vacuum. (c) Typical cyclic voltammograms of Ni(tpy) under argon or CO₂ atmosphere (2 mM Ni(tpy), 0.1 M TBAPF₆ in EA solution, 100 mV s⁻¹), a ferrocene/ferrocenium (Fc⁺/Fc) redox couple was used as an internal standard (Figure S7). (d) Schematic representation of the CsPbBr₃-Ni(tpy) photocatalyst system developed in this work: immobilizing of Ni(tpy) metal complexes onto a CsPbBr₃ NC

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Since CsPbBr₃-Ni(tpy) is formed by immobilizing Ni(tpy) on CsPbBr₃ NCs, to evaluate whether CsPbBr₃-Ni(tpy) can provide a sufficient driving force for CO₂ reduction, we determined the band structure of CsPbBr₃ and the reduction potential of the Ni(tpy) catalyst. According to the Tauc plot of $(\alpha hv)^2 vs hv$ from the UV-vis absorption spectra, the band gap (E_g) of CsPbBr₃ is approximately 2.39 eV (Figure 3a). The VB of CsPbBr₃ was also measured by the valence band XPS (Figure 3b), which displayed an edge of the maximum energy at about 1.78 eV vs. Fermi level. Because the band gap of the CsPbBr₃ as found from the Tauc plot is 2.39 eV, we can conclude that the VB and conduction band (CB) positions of CsPbBr₃ NCs are around -5.98 V and -3.59 V vs. vacuum, which is in agreement with the literature results.⁽²⁵⁾ Subsequently, we conducted the CV of Ni(tpy) under Ar and CO₂ atmospheres, respectively (as shown in Figure 3c). Under an inert atmosphere, the CV curve display two reversible electrochemical features, which can be assigned to ligand-based electrochemical processes. In its own turn, under CO₂ condition, the two electrochemical features lose reversibility and the intensity of the corresponding cathodic peaks increased significantly. The enhanced current indicates electrocatalytic activity of Ni(tpy) toward CO_{2} ⁽⁴³⁾ of which the singly reduced Ni(tpy) upon reaction with CO₂ to give some Ni-related active species (e.g., Ni-CO₂ and the Ni-CO complex).⁽²²⁾ The above results allowed us to suggest the schematics of the photocatalytic CO_2 reduction process with the CsPbBr₃-Ni(tpy) photocatalysts. As illustrated in Figure 3d, under visible-light illumination, CsPbBr₃ will absorb light and generate photoexcited electrons on the CB edge. Considering that the CsPbBr₃ NCs has a more negative CB potential than the CdS NCs, ^(22,50) and the CdS NCs can provide an efficient driving force to enable CO₂ reduction at Ni(tpy),⁽²²⁾ we can conclude that the photogenerated electrons at the CB edge of CsPbBr₃ can be swiftly injected into Ni(tpy) for CO₂ reduction.



Figure 4. Photocatalytic CO₂ reduction using CsPbBr₃-based NCs. (a) Production of gases using various photocatalysts based on the pristine CsPbBr₃, the pristine Ni(tpy) and CsPbBr₃-Ni(tpy); error bars correspond to standard deviations based on three experiments. (b) Changes in gases production as a function of the added Ni(tpy). (c) Cycling production of CH₄ and CO using CsBrBr₃-Ni(tpy). (d) Mass spectra showing ¹³CH₄ (m/z=17) and ¹³CO (m/z=29) produced over CsBrBr₃-Ni(tpy) in the photocatalytic reduction of ¹³CO₂. Conditions unless stated otherwise: 100 mW cm⁻², $\lambda > 400$ nm (see the light spectra in Figure S8), 4 h, 25 °C (5 mg photocatalysts in 5 mL of EA solution (EA/water (49:1, v:v)).

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The photocatalytic activity of the CsPbBr₃-based catalysts was assessed in CO₂-saturated EA in the presence of water. As shown in Figure 4a, the pristine CsPbBr₃ shows very low catalytic activity toward CO₂ reduction, and the pristine Ni(tpy) has no photocatalytic activity due to its inability to absorb visible light. However, when we immobilized the Ni(tpy) onto the CsPbBr₃, the photocatalytic properties of the composite were significantly improved. For the CsPbBr₃, the small PF₆⁻ ligands offer a nearly naked NC surface with low charge-transfer resistance upon stripping the OLs (detailed evidence is provided in Figure S9-S11), which allows more photogenerated electrons to reach the surface of CsPbBr₃. At the same time, Ni(tpy) can trap photogenerated electrons from CsPbBr₃ and provide efficient catalytic sites near the NC surface for CO₂ reduction. As a result, the photocatalytic activity of CsPbBr₃-Ni(tpy) was impressively high, achieving 1724 μ mol/g of CO/CH₄, which are almost 26-fold higher than that observed for the pristine CsPbBr₃. These findings strongly indicate that the immobilization of metal complexes is a powerful approach for improving the photocatalytic activity of CsPbBr₃ NCs for CO₂ reduction.

Since the photocatalytic activity of CsPbBr₃ was directly affected by Ni(tpy), we altered the amount of Ni(tpy) to explore their effect on the photocatalytic activity in CO₂ reduction. Catalysts with different Ni(tpy) loadings can be easily obtained by changing the amount of Ni(tpy) added during the immobilization. With the increase of Ni(tpy) content from 0.06 to 0.48 μ mol, the catalytic properties of CsPbBr₃-Ni(tpy) gradually increase and then approach a plateau. At the maximum (0.24 μ mol Ni(tpy)), the reduction of CO₂ to CO/CH₄ achieved the highest value of 1724 μ mol/g. We attributed this to the increased number of Ni(tpy) immobilized on the surface of CsPbBr₃, as in general, more catalytic sites can offer a higher activity. The plateau of the catalytic activity with the amount of Ni(tpy) increasing over 0.24 μ mol may result from the

redundant Ni(tpy), which will only weakly immobilize to the NC surface, and the excess of Ni(tpy) would detach from the CsPbBr₃ during the catalytic process (see the evidence provided in the supporting information, Figure S12). The increase of the Ni(tpy) concentration also promoted greater electron transfer from the CsPbBr₃ to the Ni(tpy) electron sinks, which can be verified by the quenching of the NC luminescence (Figure S13). This behavior is consistent with previous works conducted with other semiconductor-metal complex systems.⁽²⁰⁾ It suggests that Ni(tpy) are mainly immobilized onto $CsPbBr_3$ rather than physically colliding with $CsPbBr_3$ in solution. Furthermore, the maximum electron consumption rate ($R_{electron} = 2R(CO) + 8R(CH_4)$) of CsPbBr₃/GO is 29.8 µmol g⁻¹h⁻¹, and the R_{electron} of the CsPbBr₃-Ni(tpy) exhibit a higher value of 1252 µmol g⁻¹h⁻¹. The latter is an excellent result as compared to other perovskite-based photocatalysts for CO₂ reduction reported in the literature (Table S1). As to the CsPbBr₃/GO composite, although GO provides an additional transfer channel for photoexcited electrons, it lacks, most probably, effective catalytic sites. At the same time, in the case of CsPbBr₃-Ni(tpy), the Ni(tpy) can serve as the electron sink and can supply catalytic sites for a targeted reaction providing in our case a higher photocatalytic activity for the CO₂ reduction.

Figure 4c illustrates the time-dependent CO and CH₄ generation rates using CsPbBr₃-Ni(tpy) as a catalyst. There is no obvious decrease in the gas evolution rate in the first 4 h of the reaction (one cycle). This stable photocatalytic activity reduces for only less than 15 % of its initial value after repeating the above process for four cycles. We also performed some characterizations of the CsPbBr₃-Ni(tpy) photocatalysts after 2 h photocatalytic reaction (Figure S14-S16), the results indicated that the CsPbBr₃-Ni(tpy) photocatalysts could keep stable during photocatalysis. Control experiments (Figure S17) confirmed that CO₂ is the feedstock for product generation, which was verified further by isotope labeling experiments using ¹³CO₂.

When ${}^{13}CO_2$ was used as the feedstock, two major signals with *m/z* values of 29 and 17 assigned to ${}^{13}CO$ and ${}^{13}CH_4$ were detected (Figure 4d). Therefore, the generated CO and CH₄ can be attributed to the photocatalytic reduction of CO₂. In addition, for CsPbBr₃-Ni(tpy), the apparent quantum efficiency (AQE) for CO and CH₄ production under 450 nm monochromatic light was 0.23% (Figure S18). The AQE of the system correlates well with the absorption spectra of CsPbBr₃. The dependency indicates that CO and CH₄ evolution was induced by photoabsorption due to the band-gap excitation of CsPbBr₃.



Figure 5. (a) Photoluminescence (PL) quenching of CsPbBr₃ and CsPbBr₃-Ni(tpy) ($\lambda_{ex} =$ 380 nm). (b) TRPL of CsPbBr₃ and CsPbBr₃-Ni(tpy) (the scatter points were fitted using a

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biexponential decay) ($\lambda_{ex} = 380 \text{ nm}$, $\lambda_{em} = 515 \text{ nm}$). (c) The TA traces for CsPbBr₃ and CsPbBr₃-Ni(tpy) normalized to the first photoinduced absorption peak at 508 nm. (d) I-t curves plotted at 0.2 V versus Ag/AgCl under light illumination (100 mW cm⁻²).

The CsPbBr₃ becomes an efficient photosensitizer after immobilizing Ni(tpy) primarily because of the efficient electron transfer from CsPbBr₃ to Ni(tpy). To clarify the key role of Ni(tpy) in facilitating electron transfer, we analyzed the CsPbBr₃ and CsPbBr₃-Ni(tpy) samples using both steady state and time-resolved PL analyses (measurement details are given in the SI). As shown in Figure 5a, CsPbBr₃ exhibits a strong PL peak centered at approximately 515 nm upon excitation with 380 nm light. After immobilizing the Ni(tpy), the PL intensity of CsPbBr₃ is quenched. This PL quenching behavior corresponds to electron transfer from CsPbBr₃ to Ni(tpy). We then used TRPL spectroscopy to probe the electron transfer dynamics, and applied biexponential fitting to the TRPL curves. As shown in Figure 5b, the PL decay of CsPbBr₃ becomes significantly faster in the presence of Ni(tpy), and the average lifetimes of CsPbBr₃ were shortened from 47.3 ns to 5.3 ns after the immobilizing Ni(tpy). CsPbBr₃ NCs often show two lifetimes: a long PL lifetime (τ_1) that may correlate to the band-edge electron-hole radiative recombination, and a short PL lifetime (τ_2) that can be attributed to exciton recombination with the involvement of surface states or electron transfer.⁽⁵¹⁾ According to the fitting results, pristine CsPbBr₃ possesses a long lifetime (τ_1) of 52.5 ns and a short lifetime (τ_2) of 9.4 ns with amplitudes of 57.0% and 43.0%, respectively. In contrast, CsPbBr₃-Ni(tpy) has two shorter lifetimes: a long lifetime (τ_1) of 8.2 ns and a short lifetime (τ_2) of 1.7 ns with amplitudes of 20.5% and 79.5%, respectively. These results suggest that the PL decay of CsPbBr₃ mainly occurs through band-edge electron-hole radiative recombination. For CsPbBr₃-Ni(tpy), the average lifetime becomes shorter due to a smaller contribution of the long-lived and a larger

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contribution of the short-lived components. Thus, the band-edge radiative recombination is remarkably suppressed, and the photogenerated electrons in the CB of the CsPbBr₃ are swiftly injected into the Ni(tpy). The PL decay results are also in line with the decrease in the PL emission intensity. Therefore, these results corroborate that the immobilized Ni(tpy) catalysts can effectively suppress charge recombination and promote charge separation in the CsPbBr₃ photosensitizers.

TA spectroscopy can provide insights into the charge carrier dynamics through the analysis of the ultrafast excited-state decay processes. Compared with time-resolved PL, TA spectroscopy has much better time resolution. Here, we use TA spectroscopy to elucidate the relationship between the electron transfer kinetics and photocatalytic performance. The TA spectra of CsPbBr₃ and CsPbBr₃-Ni(tpy) samples were acquired with excitation by a 470 nm pump pulse, and probed at 508 nm (see the SI for a detailed description). Figure 5c shows their absorption change (ΔA) curves as a function of decay times. In the CsPbBr₃ NCs, previous researches have suggested that the exciton bleach feature in the ps-ns scale is a good reflection of electron trapping/transfer.⁽⁵²⁾ After the attachment of Ni(tpy), the average lifetime (τ_n) decreased from 4337 ps (CsPbBr₃) to 65.98 ps (CsPbBr₃-Ni(tpy)). The change of TA kinetic should be mainly result from the electron transfer, considering that CO₂ reduction happens on the Ni(tpy) site. The corresponding rate constant (k_{et}) of which can be obtained by eq 1⁽⁵³⁾

 $k_{\rm et} = 1/\tau_{\rm (CsPbBr_3-Ni(tpy))} - 1/\tau_{\rm (CsPbBr_3)}$ (1)

where $\tau_{(CsPbBr_3-Ni(tpy))}$ is the lifetime of CsPbBr_3-Ni(tpy) and $\tau_{(CsPbBr_3)}$ corresponds to the lifetime of CsPbBr_3. On the basis of their average lifetimes, the calculated k_{et} is 1.49×10^{10} s⁻¹. These results confirm that the Ni(tpy) complexes can serve as electron sinks, enabling rapid electron transfer from the CsPbBr_3 to the catalytic centers, the TA decay results are also in line with the

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decrease in the PL decay. Therefore, these results corroborate that the immobilized Ni(tpy) catalysts can effectively suppress charge recombination and promote charge separation in the CsPbBr₃ photosensitizers. Overall, the above results suggest efficient charge separation in CsPbBr₃ and the delivery of the electrons to the Ni(tpy) complexes for CO₂ reduction. In addition, the photocurrent response suggests that their photocurrent is well reproducible upon on/off cycling of the light source (Figure 5d). Compared with the CsPbBr₃, a 60% enhancement in the photocurrent response was observed for the CsPbBr₃-Ni(tpy) sample, indicating efficient charge separation in the CsPbBr₃-Ni(tpy), which is consistent with their PL and TA behaviors. Overall, the above results suggest an efficient charge separation in CsPbBr₃ and the transfer of the electrons to the Ni(tpy) complexes for CO₂ reduction.

CONCLUSIONS

In summary, a CsPbBr₃-Ni(tpy) hybrid photocatalytic system was successfully fabricated through a facile approach involving the immobilizing of Ni(tpy) complexes onto CsPbBr₃ *via* electrostatic interactions. Immobilizing the metal complexes onto CsPbBr₃ is crucial for promoting the catalytic activity of CsPbBr₃ for CO₂ reduction as it facilitates electron transfer from CsPbBr₃ to the Ni(tpy) catalytic centers. The resulting photocatalyst exhibits a high yield (1724 µmol/g) of CO and CH₄, which is approximately 26-fold higher than that of the pristine CsPbBr₃. This work has developed a method for enhancing the performance of photocatalytic CO₂ reduction by immobilizing metal complexes on perovskite NCs. The methodology we present here provides an important platform for exploring new types of catalysts based on perovskite NC systems. Further optimization of our system aiming to improving the catalytic performance can include the coupling of CsPbBr₃ NCs with more efficient catalysts and/or tuning the perovskite material compositions.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website at <u>http://pubs.acs.org</u>. See Supporting Information for material synthesis, characterization methods, and control experiments.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- White, J. L.; Baruch, M. F.; Pander, J. E.; Hu, Y.; Fortmeyer, I. C.; Park, J. E.; Zhang, T.; Liao, K.; Gu, J.; Yan, Y.; Shaw, T. W.; Abelev, E.; Bocarsly, A. B. Light-Driven Heterogeneous Reduction of Carbon Dioxide: Photocatalysts and Photoelectrodes. *Chem. Rev.* 2015, *115*, 12888-12935.
- Inoue, T.; Fujishima, A.; Konishi, S.; Honda, K. Photoelectrocatalytic Reduction of Carbon Dioxide in Aqueous Suspensions of Semiconductor powders. *Nature* 1979, 277, 637-638.
- (3) Sakimoto, K. K.; Wong, A. B.; Yang, P. Self-Photosensitization of Nonphotosynthetic Bacteria for Solar-to-Chemical Production. *Science* 2016, 351, 74-77.
- (4) Long, R.; Li, Y.; Liu, Y.; Chen, S.; Zheng, X.; Gao, C.; He, C.; Chen, N.; Qi, Z.; Song, L.; Jiang, J.; Zhu, J.; Xiong, Y. Isolation of Cu Atoms in Pd Lattice: Forming Highly Selective Sites for Photocatalytic Conversion of CO₂ to CH₄. J. Am. Chem. Soc. 2017, 139, 4486-4492.
- Wang, J.; Xia, T.; Wang, L.; Zheng, X.; Qi, Z.; Gao, C.; Zhu, J.; Li, Z.; Xu, H.; Xiong, Y. Enabling Visible-Light-Driven Selective CO₂ Reduction by Doping Quantum Dots: Trapping Electrons and Suppressing H₂ Evolution. *Angew. Chem., Int. Ed.* 2018, *57*, 16447-16451.
- (6) Cui, X.; Wang, J.; Liu, B.; Ling, S.; Long, R.; Xiong, Y. Turning Au Nanoclusters Catalytically Active for Visible-Light-Driven CO₂ Reduction through Bridging Ligands. J. Am. Chem. Soc. 2018, 140, 16514-16520.
- (7) Habisreutinger, S. N.; Schmidt-Mende, L.; Stolarczyk, J. K. Photocatalytic Reduction of CO₂ on TiO₂ and Other Semiconductors. *Angew. Chem., Int. Ed.* 2013, *52*, 7372-7408.
- (8) Kuriki, R.; Sekizawa, K.; Ishitani, O.; Maeda, K. Visible-Light-Driven CO₂ Reduction with Carbon Nitride: Enhancing the Activity of Ruthenium Catalysts. *Angew. Chem., Int. Ed.* 2015, *54*, 2406-2409.
- (9) Wang, D.; Huang, R.; Liu, W.; Sun, D.; Li, Z. Fe-Based MOFs for Photocatalytic CO₂ Reduction: Role of Coordination Unsaturated Sites and Dual Excitation Pathways. ACS Catal. 2014, 4, 4254-4260.
- (10) Froehlich, J. D.; Kubiak, C. P. The Homogeneous Reduction of CO₂ by [Ni(cyclam)]⁺: Increased Catalytic Rates with the Addition of a CO Scavenger. J. Am. Chem. Soc. 2015, 137, 3565-3573.

- (11) Takeda, H.; Ohashi, K.; Sekine, A.; Ishitani, O. Photocatalytic CO₂ Reduction Using Cu(I) Photosensitizers with a Fe(II) Catalyst. J. Am. Chem. Soc. 2016, 138, 4354-4357.
- (12) Rao, H.; Schmidt, L. C.; Bonin, J.; Robert, M. Visible-Light-Driven Methane Formation from CO₂ with a Molecular Iron Catalyst. *Nature* 2017, 548, 74-77.
- (13) Dalle, K. E.; Warnan, J.; Leung, J. J.; Reuillard, B.; Karmel, I. S.; Reisner, E. Electro- and Solar-Driven Fuel Synthesis with First Row Transition Metal Complexes. *Chem. Rev.* 2019, 119, 2752-2875.
- (14) Berardi, S.; Drouet, S.; Francàs, L.; Gimbert-Suriñach, C.; Guttentag, M.; Richmond, C.; Stoll, T.; Llobet, A. Molecular Artificial Photosynthesis. *Chem. Soc. Rev.* 2014, 43, 7501-7519.
- (15) Gao, C.; Wang, J.; Xu, H. X.; Xiong, Y. Coordination Chemistry in the Design of Heterogeneous Photocatalysts. *Chem. Soc. Rev.* 2017, *46*, 2799-2823.
- (16) Kumar, B.; Llorente, M.; Froehlich, J.; Dang, T.; Sathrum, A.; Kubiak, C. P. Photochemical and Photoelectrochemical Reduction of CO₂. *Annu. Rev. Phys. Chem.* **2012**, *63*, 541.
- (17) Takeda, H.; Cometto, C.; Ishitani, O.; Robert, M. Electrons, Photons, Protons and Earth-Abundant Metal Complexes for Molecular Catalysis of CO₂ Reduction. *ACS Catal.* 2017, 7, 70-88.
- (18) Arias-Rotondo, D. M.; McCusker, J. K. The Photophysics of Photoredox Catalysis: a Roadmap for Catalyst Design. *Chem. Soc. Rev.* **2016**, *45*, 5803-5820.
- (19) Wu, H. L.; Li, X. B.; Tung, C. H.; Wu, L. Z. Semiconductor Quantum Dots: An Emerging Candidate for CO₂ Photoreduction. *Adv. Mater.* **2019**, *31*, 1900709.
- (20) Kuehnel, M. F.; Sahm, C. D.; Neri, G.; Lee, J. R.; Orchard, K. L.; Cowan, A. J.; Reisner, E. ZnSe Quantum Dots Modified with a Ni(cyclam) Catalyst for Efficient Visible-Light Driven CO₂ Reduction in Water. *Chem. Sci.* 2018, *9*, 2501-2509.
- (21) Lian, S.; Kodaimati, M. S.; Dolzhnikov, D. S.; Calzada, R.; Weiss, E. A. Powering a CO₂ Reduction Catalyst with Visible Light through Multiple Sub-Picosecond Electron Transfers from a Quantum Dot. *J. Am. Chem. Soc.* **2017**, *139*, 8931-8938.
- (22) Kuehnel, M. F.; Orchard, K. L.; Dalle, K. E.; Reisner, E. Selective Photocatalytic CO₂ Reduction in Water through Anchoring of a Molecular Ni Catalyst on CdS Nanocrystals. *J. Am. Chem. Soc.* 2017, *139*, 7217-7223.

- (23) Shamsi, J.; Urban, A. S.; Imran, M.; De Trizio, L.; Manna, L. Metal Halide Perovskite Nanocrystals: Synthesis, Post-Synthesis Modifications, and Their Optical Properties. *Chem. Rev.* 2019, *119*, 3296-3348.
- (24) Akkerman, Q. A.; Raino, G.; Kovalenko, M. V.; Manna, L. Genesis. Challenges and Opportunities for Colloidal Lead Halide Perovskite Nanocrystals. *Nat. Mater.* 2018, 17, 394-405.
- (25) Xu, Y.; Yang, M.; Chen, B.; Wang, X.; Chen, H.; Kuang, D.; Su, C. A CsPbBr₃ Perovskite Quantum Dot/Graphene Oxide Composite for Photocatalytic CO₂ Reduction. *J. Am. Chem. Soc.* 2017, *139*, 5660-5663.
- (26) Ou, M.; Tu, W.; Yin, S.; Xing, W.; Wu, S.; Wang, H.; Wan, S.; Zhong, Q.; Xu, R. Amino-Assisted Anchoring of CsPbBr₃ Perovskite Quantum Dots on Porous g-C₃N₄ for Enhanced Photocatalytic CO₂ Reduction. *Angew. Chem. Int. Ed.* **2018**, *57*, 13570-13574.
- (27) Wu, Li. Y.; Mu, Y. F.; Guo, X. X.; Zhang, W.; Zhang, Z. M.; Zhang, M.; Lu, T. B. Encapsulating Perovskite Quantum Dots in Iron-Based Metal-Organic Frameworks (MOFs) for Efficient Photocatalytic CO₂ Reduction. *Angew. Chem. Int. Ed.* **2019**, *58*, 9491-9495.
- (28) Zhu, X.; Lin, Y.; Sun, Y.; Beard, M. C.; Yan, Y. Lead-Halide Perovskites for Photocatalytic α-Alkylation of Aldehydes. J. Am. Chem. Soc. 2017, 141, 733-738.
- (29) Cardenas-Morcoso, D.; Gualdron-Reyes, A. F.; Vitoreti, A. B. F.; Garcia-Tecedor, M.; Yoon, S. J.; de la Fuente, M. S.; Mora-Sero, I.; Gimenez, S. Photocatalytic and Photoelectrochemical Degradation of Organic Compounds with All-Inorganic Metal Halide Perovskite Quantum Dots. J. Phys. Chem. Lett. 2019, 103, 630-636.
- (30) Zhou, L.; Xu, Y. F.; Chen, B. X.; Kuang, D. B.; Su, C. Y. Synthesis and Photocatalytic Application of Stable Lead-Free Cs₂AgBiBr₆ Perovskite Nanocrystals. *Small* 2018, 14, 1703762.
- (31) Park, S.; Chang, W. J.; Lee, C. W.; Park, S.; Ahn, H.-Y.; Nam, K. T. Photocatalytic Hydrogen Generation from Hydriodic Acid Using Methylammonium Lead Iodide in Dynamic Equilibrium with Aqueous Solution. *Nat. Energy* **2016**, *2*, 16185.
- (32) Hong, Z.; Chong, W. K.; Ng, A. Y. R.; Li, M.; Ganguly, R.; Sum, T. C.; Soo, H. S. Hydrophobic Metal Halide Perovskites for Visible-Light Photoredox C-C Bond Cleavage and Dehydrogenation Catalysis. *Angew. Chem. Int. Ed.* **2019**, *58*, 3456-3460.

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- (33) Wang, L.; Xiao, H.; Cheng, T.; Li, Y.; Goddard III, W. A. Pb-Activated Amine-Assisted Photocatalytic Hydrogen Evolution Reaction on Organi-Inorganic Perovskites. J. Am. Chem. Soc. 2018, 140, 1994-1997.
- (34) Zhang, Z.; Liang, Y.; Huang, H.; Liu, X.; Li, Q.; Chen, L.; Xu, D. Stable and Highly Efficient Photocatalysis with Lead-Free Double-Perovskite of Cs₂AgBiBr₆. *Angew. Chem. Int. Ed.* 2019, *58*, 7263-7267.
- (35) Huang, H.; Yuan, H.; Janssen, K. P. F.; Solís-Fernández, G.; Wang, Y.; Tan, C. Y. X.; Jonckheere, D.; Debroye, E.; Long, J.; Hendrix, J.; Hofkens, J.; Steele, J. A.; Roeffaers, M. B. J. Efficient and Selective Photocatalytic Oxidation of Benzylic Alcohols with Hybrid Organic-Inorganic Perovskite Materials. *ACS Energy Lett.* 2018, *3*, 755-759.
- (36) Wu, Y.; Wang, P.; Zhu, X.; Zhang, Q.; Wang, Z.; Liu, Y.; Zou, G.; Dai, Y.; Whangbo, M.-H.; Huang, B. Composite of CH₃NH₃PbI₃ with Reduced Graphenme Oxide as a Highly Efficient and Stable Visible-Light Photocatalyst for Hydrogen Evlution in Aqueous HI Solution. *Adv. Mater.* 2018, *30*, 1704342.
- (37) Zhao, Z.; Wu, J.; Zheng, Y.Z.; Li, N.; Li, X.; Tao, X. Ni₃C-Decorated MAPbI₃ as Visible-Light Photocatalyst for H₂ Evolution from HI Splitting. *ACS Catal.* **2019**, *9*, 8144-8152.
- (38) Wang, H.; Wang, X.; Chen, R.; Zhang, H.; Wang, X.; Wang, J.; Zhang, J.; Mu, L.; Wu, K.; Fan, F.; Zong, X.; Li, C. Promoting Photocatalytic H₂ Evolution on Organic-Inorganic Hybrid Perovskite Nanocrystals by Simultaneous Dual-Charge Transportation Modulation. *ACS Energy Lett.* 2019, *4*, 40-47.
- (39) Slavney, A. H.; Hu, T.; Lindenberg, A. M.; Karunadasa, H. I. A Bismuth-Halide Double Perovskite with Long Carrier Recombination Lifetime for Photovoltaic Applications. J. Am. Chem. Soc. 2016, 138, 2138-2141.
- (40) Zhu, X.; Lin, Y.; San Martin, J.; Sun, Y.; Zhu, D.; Yan, Y. Lead Halide Perovskites for Photocatalytic Organic Synthesis. *Nat. Commun.* 2019, 10, 2843.
- (41) Francke, R.; Schille, B.; Roemelt, M. Homogeneously Catalyzed Electroreduction of Carbon Dioxide-Methods, Mechanisms, and Catalysts. *Chem. Rev.* **2018**, *118*, 4631-4701.
- (42) Qiao, J.; Liu, Y.; Hong, F.; Zhang, J. A Review of Catalysts for the Electroreduction of Carbon Dioxide to Produce Low-Carbon Fuels. *Chem. Soc. Rev.* 2014, 43, 631-675.

- (43) Elgrishi, N.; Chambers, M. B.; Artero, V.; Fontecave, M. Terpyridine Complexes of First Row Transition Metals and Electrochemical Reduction of CO₂ to CO. *Phys. Chem. Chem. Phys.* 2014, *16*, 13635-13644.
- (44) Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.; Caputo, R.; Hendon, C. H.; Yang, R. X.; Walsh, A.; Kovalenko, M. V. Nanocrystals of Cesium Lead Halide Perovskites (CsPbX₃, X = Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. *Nano Lett.* 2015, *15*, 3692-3696.
- (45) Nag, A.; Kovalenko, M. V.; Lee, J. S.; Liu, W.; Spokoyny, B.; Talapin, D. V. Metal-Free Inorganic Ligands for Colloidal Nanocrystals: S²⁻, HS⁻, Se²⁻, HSe⁻, Te²⁻, Hte⁻, TeS₃²⁻, OH⁻, and NH₂⁻ as Surface Ligands. *J. Am. Chem. Soc.* **2011**, *133*, 10612-10620.
- (46) Li, J.; Xu, L.; Wang, T.; Song, J.; Chen, J.; Xue, J.; Dong, Y.; Cai, B.; Shan, Q.; Han, B.; Zeng, H. 50-Fold EQE Improvement up to 6.27% of Solution-Processed All-Inorganic Perovskite CsPbBr₃ QLEDs via Surface Ligand Density Control. *Adv. Mater.* 2017, *29*, 1603885.
- (47) Lu, X.; Tuan, H.-Y.; Chen, J.; Li, Z.-Y.; Korgel, B. A.; Xia, Y. Mechanistic Studies on the Galvanic Replacement Reaction between Multiply Twinned Particles of Ag and HAuCl₄ in an Organic Medium. *J. Am. Chem. Soc.* **2007**, *129*, 1733-1742.
- (48) Pan, J.; Quan, L. N.; Zhao, Y. B.; Peng, W.; Murali, B.; Sarmah, S. P.; Yuan, M. J.; Sinatra, L.; Alyami, N. M.; Liu, J. K.; Yassitepe, E.; Yang, Z. Y.; Voznyy, O.; Comin, R.; Hedhili, M. N.; Mohammed, O. F.; Lu, Z. H.; Kim, D. H.; Sargent, E. H.; Bakr, O. M. Highly Efficient Perovskite-Quantum-Dot Light-Emitting Diodes by Surface Engineering. *Adv. Mater.* 2016, 28, 8718-8725.
- (49) Guyot-Sionnest, P.; Lhuillier, E.; Liu, H. A Mirage Study of CdSe Colloidal Quantum Dot Films, Urbach Tail, and Surface States. *J. Chem. Phys.* **2012**, *137*, 154704.
- (50) Chen, J.; Dong, C.; Idriss, H.; Mohammed, O. F.; Bakr, O. M. Metal Halide Perovskites for Solar-to-Chemical Fuel Conversion. *Adv. Energy Mater.* **2019**, 1902433.
- (51) Lightcap, I. V.; Kamat, P. V. Fortification of CdSe Quantum Dots with Graphene Oxide.
 Excited State Interactions and Light Energy Conversion. J. Am. Chem. Soc. 2012, 134, 7109-7116.

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Soc. 2015, 137, 12792-12795.

Am. Chem. Soc. 2006, 128, 2385-2393.

from

(52) Wu, K.; Liang, G.; Shang, Q.; Ren, Y.; Kong, D.; Lian, T. Ultrafast Interfacial Electron and

(53) Robel, I.; Subramanian, V.; Kuno, M.; Kamat, P. V. Quantum Dot Solar Cells. Harvesting

Light Energy with CdSe Nanocrystals Molecularly Linked to Mesoscopic TiO₂ Films. J.

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