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Inorganic Colloidal Perovskite Quantum Dots Realizing Robust Solar CO₂ Reduction

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Dedication ((optional))

Abstract: Inorganic perovskite quantum dots as optoelectronic materials have attracted enormous attention in light harvesting and emitting devices. However, photocatalytic conversion based on inorganic perovskite halides has not been reported. Herein, we have synthesized colloidal quantum dots (QDs, 3–12 nm) of cesium lead halide perovskites (CsPbBr₃) as newcomer photocatalytic materials. The bandgap energies and photoluminescence (PL) spectra are tunable over the visible spectral region by quantum size effects on an atomic scale. The increased carrier lifetime revealed by time-resolved PL spectra, indicating the efficient electron-hole separation and transfer. As expect, the CsPbBr₃ QDs with the highly selectivity over 99% achieve an efficient yield rate of 20.9 μ mol/g towards solar CO₂ reduction. This work has opened a new avenue for inorganic colloidal perovskite materials as efficient photocatalysts to convert CO₂ into valuable fuels.

The climate change and increasing local conflict as two important issues are rooted in the unsustainable utilization of fossil fuels accompanied with release of greenhouse gas CO_2 .^[1] The conversion of CO_2 reduction into energy-rich chemicals presents promise as a viable CO_2 utilization process, not only reducing CO_2 emission, but also decreasing the energy shortage.^[2] In this regard, artificial photosynthesis based the conversion of CO_2 and water into valuable fuels by use of photocatalysts at room temperature and ambient pressure, has been regarded as one of the most promising and compelling strategies for simultaneously solving the energy and environmental problems.^[3]

To date, many UV-, or visible-light photocatalytic systems for CO₂ conversion have been developed by use of various materials, such as metal oxides (e.g. TiO₂, Cu₂O, WO₃, Bi₂WO₆, Zn₂GeO₄, ZnGa₂O₄), nitrides (e.g. C₃N₄, GaN, (Zn_{1+x}Ge)(N₂O_x)), sulfides (e.g. CdS, ZnS and Cu₂ZnSnS₄) and phosphides (e.g. InP, GaP).^[4,5] However, the intrinsic limitations (e.g. narrow light harvesting, complex synthesis processes and short lifetime of photoinduced charges) have been existed in these catalysts with poor selectivity, low conversion efficiency, and low stability.^[4,5]

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Thus, it is an urgent need to develop highly efficient and stable visible-light photocatalysts for CO_2 conversion.

To address the limitation of these materials for solar-to-fuel conversion, the state-of-the-art accomplishments have been conducted through the design of highly active photocatalysts from the charge separation and transport, light harvesting, and CO2 activation. However, it is essential to seek novel candidates for soalr CO2 conversion. Recently, organicinorganic lead halides MAPbX₃ (MA = CH₃NH₃, X = CI, Br, and I) as interesting optoelectronic materials are reported on highly efficient photovoltaic devices with certified power conversion efficiencies.^[6] It is notable that methylammonium lead iodide material has been applied to conduct photocatalytic hydrogen generation.^[69] However, it is instable in humid conditions as a critical environment.^[6] As a result, fabricating inorganic perovskite halide nanocrystals with high stability is highly desirable and imperative for efforts to achieve highly efficient solar CO₂ conversion into fuels.

Inspired by these points, the inorganic perovskite halide nanocrystals present a new class of photochemical conversion materials with the combined advantages of outstanding optical signatures and high stability. Especially, colloidal semiconductor quantum dots (QDs), are being reported intensively as the promising optoelectronic materials by virtue of the quantum confinement effect.^[7] However, it is an essential role for the atomic-level design and control of the size-dependent photocatalytic system by precisely colloidal chemistry.^[8] It is noteworthy that the cesium lead halide (CsPbBr₃) is a promising photocataytic semiconductor that has a large portion of the solar spectrum and a suitable band gap.^[7] With all of these advantages, it is rather imperative to fabricate CsPbBr₃ QDs. Herein, the CsPbBr₃ QDs were put forward as an ideal candidate for in-depth understanding of size-dependent CO₂ reduction. The bandgap energies and photoluminescence (PL) spectra are tunable over the visible spectral region by quantum size-effects. The increased carrier lifetime revealed by time-resolved PL spectra, accounting for the improved electron-hole separation efficiency. As a result, the CsPbBr₃ QDs with an optimum size achieve high photochemical conversion efficiency from solar CO₂ reduction reaction.

The colloidal CsPbBr₃ QDs have been synthesized through the solution phase synthesis strategy (Figure 1a) by use of inexpensive commercial precursors, taking advantage of the ionic nature of the chemical bonding in these compounds. First, Cs⁺, Pb²⁺, and Br⁻ ions were selected as ion sources to dissolve in the system, while oleylamine (OAm) and oleic acid (OA) were applied as surface ligands. Then, controlling the reaction of Cs-oleate with a Pb(II)-halide, the CsPbBr₃ QDs were obtained by the arrested precipitation of Cs⁺, Pb²⁺, and Br⁻ ions (see experimental section). The XRD pattern (Figure S1) for the accumulated powder sample could be

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readily indexed to pure CsPbBr₃ phase. From TEM images (Figure 1bc), the average size of the cubic-shaped CsPbBr₃ QDs prepared at 170 °C is ranged around 8.5 nm. As shown in Figure 1d, the lattice spacing can be indexed to the (100) and (010) planes. To check the chemical compositions, high-resolution spectra of the core levels of Cs 3d, Pb 4f, and Br 3d were recorded (Figure S2). The peaks at 723.8 eV and 737.5 eV can be attributed to the Cs $3d_{3/2}$ and Cs $3d_{5/2}$ level spectra of the CsPbBr₃ QDs.^[7a] Besides, the peaks at 138.6 eV and 143.9 eV can be indexed to the Pb $4f_{7/2}$ and Pb $4f_{5/2}$ level spectra of the CsPbBr₃ QDs.^[7a] In addition, the peak at 68.5 eV can be indexed to the Br 3d core level spectra of the CsPbBr₃ QDs.^[7a] These results exhibits that the Cs, Pb, and Br atoms are effectively and uniformly incorporated into the CsPbBr₃ QDs.



Figure 1. (a) Schematic of solution phase synthesis of colloidal CsPbBr₃ QDs. (bcd) TEM and HRTEM images and illustration of crystalline structure of CsPbBr₃ (Cs: green sphere, Pb: yellow sphere, Br: red sphere).

Generally, the colloidal semiconductor quantum dots exhibit the intrinsical quantum size effects.^[7] Herein, the perovskite QDs with the tunable particle size have also been obtained by adjusting the reaction temperatures. As shown in Figure 2, the average sizes of the as-obtained CsPbBr₃ QDs operated at 140, 155, 170 and 185 °C are ranged around 3.8 ± 0.3 , 6.1 ± 0.3 , 8.5 ± 0.3 and 11.6 ± 0.3 nm, respectively. The size of the CsPbBr₃ QDs increases as the reaction temperature is increased. In this regard, the optical absorption and photoluminescence spectra of



Figure 2. TEM images of CsPbBr₃ QDs with different particle sizes, (a) 3.8 nm, (b) 6.1 nm, (c) 8.5 nm and (d) 11.6 nm.



Figure 3. Quantum-size effects in (a) UV-Vis absorption spectra and (b) bandgap structures of CsPbBr₃ QDs with different particle sizes, (i) 3.8 nm, (ii) 6.1 nm, (iii) 8.5 nm and (iv) 11.6 nm, as well as (d) the calculated band structure and (e) calculated densities of states diagrams of bulk CsPbBr₃ and CsPbBr₃ QDs.

CsPbBr₃ QDs can be tuned over the visible spectral region by adjusting their particle size. From the UV-vis absorption spectra, the adsorption edges of the CsPbBr3 QDs shifted the longer wavelength in the visible light region with the increasing particle size (Figure 3). To verify this point, the first-principle calculations were achieved. As show in Figure 3c, the calculated the band gap energy (E₉) of the CsPbBr₃ QDs was approximately 2.39 eV To understand the advantage of the CsPbBr3 QDs, the calculated densities of states (DOS) of bulk CsPbBr3 and atomic CsPbBr₃ QDs slab, reveal the typical semiconductor characteristic with the narrow bandgap (Figure 3de/Figure S3). In details, the upper region in valence band of the CsPbBr₃QDs is constituted by the Cs-5p, Pb-6s and Br-4p orbitals and the region in conduction band of CsPbBr₃ QDs is composed of the Cs-5p, Pb-6p and Br-4p orbitals. In comparison of bulk CsPbBr₃ with big size and severe aggregation (Figure S3), the increased DOS at the conduction band edge compared with the bulk counterpart, demonstrating that more photogenerated carriers could be effectively transported to the conduction band minimum of the CsPbBr₃ QDs, corresponding the increased valence band maximum.^[9] Therefore, the photogenerated electrons could

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easily be excited into the conduction band under solar light irradiation, implementing the effective photochemical conversion. In addition, the typical photoluminescence peak of the CsPbBr₃ QDs shifted to longer wavelength sides when the size of QDs was increased (Figure S4/S5). Based on above-mentioned results, we can conclude that the quantum size-effects can effectively regulate the band gap structure and improve the optical absorption of the CsPbBr₃ QDs.

To evaluate the roles of the CsPbBr₃ QDs upon photocatalysis, it is essential to drive the photochemical CO₂ conversion. The CO₂ photoreduction experiments were carried out in ethyl acetate/H₂O system under a 300 W Xe lamp with a standard AM 1.5G filter, and the predominant reaction products analyzed by gas chromatography (GC) were CO, CH₄ and H₂. The CO, CH₄ and H₂ yields gradually increased with the photolysis time, and the total yields of CO (R_{CO}), CH₄ (R_{CH4}) and H₂ (R_{H2}) obtained in the experiment after 8 h irradiation were 34.1±0.1, 12.2±0.1 and 0.80±0.03 µmol g⁻¹, corresponding to approximately 4.3, 1.5 and 0.1 μ mol g⁻¹ h⁻¹ of the formation rates of CO, CH₄ and H₂, respectively (Figure 4a). All the product generation presents the almost linear growth with the increased time. According to the equation $(R_{electron}=2R_{CO}+8R_{CH4}+2R_{H2})$, the averaged electron yield (R_{electron}) rate for the CsPbBr₃ QDs is 20.9 µmol g⁻¹ h⁻¹ during the whole reaction. Such a high product formation rate of the CsPbBr₃ QDs is much larger than that of previously reported WO₃, CdS, Cu₂S and PbS/TiO₂, demonstrating the superior catalytic activity of CsPbBr₃ QDs.^[4c,10] To investigate the origin of the CO and CH₄ produced during solar CO₂ reduction reaction, the experiments demonstrated that there was no detectable product generation in the dark or in the absence of catalysts. At Ar atmosphere, a certain amount of CO and CO₂ was obtained, indicating that the partial photooxidation of ethyl acetate.^[71] Furthermore, isotope-labeling experiment with ¹³CO₂ was used through the analysis of GC-MS spectra (Figure S6). Based on above analysis, the origin of CO and CH₄ generated was confirmed to come from CO2 under artificial irradiation with CsPbBr₃ QDs.



Figure 4. Solar CO₂ reduction into fuels under 300 W Xe lamp irradiation for CsPbBr₃ QDs, (a) 8.5 nm CsPbBr₃ QDs and (b) tunable CsPbBr₃ QDs with different particle sizes.

Since the colloidal quantum dots have emerged as promising materials for this application due to the ability to tailor their properties through size modulation.^[7] To construct the bridge of the quantum size-effect and solar-driven CO_2 reduction, the tunable CsPbBr₃ QDs with various particle sizes have been conducted the CO_2 photoreduction tests. As shown in Figure 4b, the 8.5 nm CsPbBr₃ QDs achieved the highest yields of CO, CH₄ and H₂ obtained after 8 h solar light irradiation. Frankly, the 8.5 nm CsPbBr₃ QDs possess the strong optical absorption ability,

the ideal surface area and reaction sites, facilitating the charge transfer to the surface, shortening the charge transfer pathways and simultaneously suppressing the electron-hole recombination. In general, the size decreasing behavior leads to severe aggregation while the large size also decrease the surface area,^[7] influencing the optical absorption and charge transfer and separation.^[4,5] Thus, the optimization of the particle size plays a pivot role upon the enhancement of solar CO₂ reduction.

In this ethyl acetate/water system, the water plays a role as a proton source and ethyl acetate was chosen as the solvent due to high CO₂ solubility.^[11] A large amount of water is detrimental to the stability of the CsPbBr₃ QDs (Figure S7). However, there is no obvious influence upon the stability of the CsPbBr₃ QDs in the solvent of ethyl acetate with a small amount of water (Figure S7). Notably, based on the calculation for solar CO₂ reduction (selectivity= $(2R_{CO}+8R_{CH4})/R_{electron}x100\%)$, the selectivity for solar CO₂ reduction was impressively over 99%, indicating the efficiently suppressed H₂ generation in the ethyl acetate/water system. In addition, there is no apparent change upon the morphology and the crystalline structure of the CsPbBr₃ QDs before and after photocatalysis (Figure S8/S9), confirming the excellent photostability in the ethyl acetate/water system, giving prospective signs for practical solar fuels production.



Figure 5. Time-resolved PL decays for excitation at 370 nm of tunable CsPbBr₃ QDs with different particle sizes and band diagram of solar CO₂ reduction into fuels on CsPbBr₃ QDs.

To gain an in-depth understanding of the photoexcited charge separation efficiency, we resorted to the time-resolved photoluminescence spectra for tracking in real time the charge carrier dynamics. Through fitting the decay spectra, the lifetime of 8.5 nm QDs (9.7 ± 0.2 ns) is longer than that of 3.8 nm QDs (6.6 ± 0.2 ns), 6.1 nm QDs (7.8 ± 0.2 ns) and 11.6 nm QDs (8.9 ± 0.2 ns). The longest PL lifetime implies the lowest charge carrier recombination rate for 8.5 nm QDs. From the electron dynamics perspective, it is essential to infer that such a dramatic lifetime increase in the CsPbBr₃ QDs accounts for the enhanced conversion efficiency.^[12] Therefore, the critical advance is the use of CsPbBr₃ QDs to achieve the highest performance of CO₂ conversion.

To in-depth elucidate the pertinent mechanisms of solardriven CO_2 reduction, it is worthy to constructing the band diagram of the CsPbBr₃ QDs. From the absorbance data using the Kubelka-Munk equation, the optical bandgap energy of the 8.5 nm CsPbBr₃ QDs was determined to be 2.43 eV. To determine the valence band maximum position of the asobtained CsPbBr₃ QDs, ultraviolet photoelectron spectroscopy measurement was performed (Figure S10). The valence band maximum position was determined to be -5.5 eV with respect to the vacuum level. From the determined optical bandgap and the

valence band maximum position, the conduction band minimum position was determined to be - 3.1 eV with respect to the vacuum level. From the determined optical bandgap and the valence band maximum position, the conduction band minimum and valence band maximum from the constructed band diagram of the CsPbBr₃ QDs (Figure 5) corresponded to -1.03 V and 1.4 V versus the normal hydrogen electrode (NHE) at pH=0, which is consistent with the previous reports.^[7] As a results, the reduction potential of the CsPbBr₃ QDs becomes more negative than that of $E^{\circ}(CO_2/CO) = -0.52$ V vs NHE and $E^{\circ}(CO_2/CH_4) = -$ 0.24 V vs NHE,^[4] indicating that the photogenerated electrons can react with adsorbed CO₂ and H₂O to produce CO and CH₄ (Figure 4). Currently, the photogenerated holes in the valence band oxidize water to produce oxygen and protons via the halfreaction $H_2O \rightarrow 1/2O_2 + 2H^+ + 2e^-$ ($E^0(O_2/H_2O) = 0.82$ V vs NHE).^[4] The in-situ formed O₂ evolution was observed in this system (Figure S11), revealing that water could efficiently act as the electron donor of the photogenerated holes. Based on the thermodynamic and experimental analysis, the CO, CH₄ and H₂ generation and O₂ evolution in this photocatalytic system demonstrates that the photogenerated electrons and holes simultaneously participated the respective reduction and oxidation reactions, hence giving prospective signs for solar CO₂ reduction to valuable fuels by use of the CsPbBr₃ QDs.

In summary, we have successfully synthesized colloidal quantum dots of inorganic cesium lead halide perovskites. The bandgap energies and photoluminescence spectra are tunable over the visible spectral region by quantum size effects on an atomic scale. The increased carrier lifetime revealed by timeresolved PL spectra, suppressing the detrimental electron-hole recombination, thereby accounting for the improved electronhole separation efficiency. As a result, the CsPbBr₃ QDs with the highly selectivity over 99% achieve an efficient yield rate of 20.9 µmol g⁻¹ for solar CO₂ reduction. This work not only provides a deeper understanding of the electron-transfer mechanism involved in inorganic colloidal perovskite materials as efficient photocatalysts but also should open a new avenue and stimulate further studies toward developing more efficient visible-lightresponsive colloidal perovskite quantum dots for CO_2 photoreduction utilizing solar energy.

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Keywords: Colloidal perovskite quantum dots • CsPbBr₃• quantum size effects • solar fuels • solar CO₂ reduction

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Layout 1:

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 $CsPbBr_3$ quantum dots as newcomer photocatalytic materials achieve an efficient yield rate and the highly selectivity over 99% for solar CO_2 reduction.



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