UDC 699.871

THE ROLE OF SOME PEROVSKITE MATERIALS IN THE PHOTOCATALYTIC REDUCTION OF CARBON DIOXIDE

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Abstract. *Perovskite materials, particularly due to their ability to tune structural and electronic properties, are widely used in energy conversion applications. These materials exhibit high efficiency in environmental protection-oriented photocatalytic reactions, such as CO_2 reduction and water splitting. The major advantage of perovskite materials lies in their ability to undergo significant structural changes and accommodate various cations. This property allows for the optimization of their photocatalytic activity. Additionally, perovskites have the ability to absorb a broad spectrum of light, which enhances energy production in photocatalytic processes. Furthermore, their performance is improved through combinations and ion doping methods that regulate their zone structures. While perovskite materials show better results than traditional methods in CO_2 reduction, challenges remain, though strategies are being developed to overcome these limitations.*

Xülasə. *Perovskit materialları, xüsusilə onların strukturunun və elektron xüsusiyyətlərinin tənzimlənə bilməsi səbəbindən enerji çevrilməsi tətbiqlərində geniş istifadə olunur. Bu materiallar, CO_2-nin azaldılması və suyun parçalanması kimi ətraf mühitin qorunmasına yönəlmiş fotokatalitik reaksiyalarda yüksək effektivliyə malikdir. Perovskit materiallarının ən böyük üstünlüyü, onların*

kristal quruluşunun geniş dəyişikliklərə məruz qalması və müxtəlif katyonları qəbul etmə qabiliyyətidir. Bu xüsusiyyət, onların fotokatalitik fəaliyyətini optimallaşdırmağa imkan verir. Ayrıca, perovskit materialları geniş spektrli işıq udma qabiliyyətinə malikdir, bu da onların fotokatalitik proseslərdə enerji istehsalını artırır. Bundan əlavə, perovskit materiallarının birləşməsi, ion doping metodları ilə zona quruluşlarının tənzimlənməsi kimi xüsusiyyətlər onların performansını artırmağa kömək edir. Perovskit materiallarının tətbiqi CO_2 azaldılması ilə bağlı ənənəvi metodlardan daha üstün nəticələr verə bilir, lakin hələ də bəzi məhdudiyyətlər mövcuddur, ancaq bu məhdudiyyətləri aradan qaldırmaq üçün müxtəlif strategiyalar inkişaf etdirilməkdədir.

Аннотация. *Перовскитные материалы, особенно из-за их способности регулировать структуру и электронные характеристики, широко используются в приложениях по преобразованию энергии. Эти материалы обладают высокой эффективностью в фотокаталитических реакциях, направленных на охрану окружающей среды, таких как редукция CO_2 и водородное распадение. Главное преимущество перовскитных материалов заключается в их способности подвергать кристаллическую структуру значительным изменениям и принимать различные катионы. Эта характеристика позволяет оптимизировать их фотокаталитическую активность. Также перовскитные материалы обладают способностью поглощать широкий спектр света, что способствует увеличению производства энергии в фотокаталитических процессах. Кроме того, их комбинации, такие как регулировка структуры зон с помощью ионного легирования, помогают улучшить их производительность. Применение перовскитных материалов может дать более высокие результаты по снижению CO_2 по сравнению с традиционными методами, но все еще существуют определенные ограничения, однако разрабатываются различные стратегии для их преодоления.*

Key words**:** *perovskite materials, CO_2 reduction, photocatalysis, energy conversion, environmental protection*

Açar sözlər**:** *perovskit materiallar, CO_2 reduksiyası, fotokataliz, enerji çevrilməsi, ətraf mühitin qorunması*

Ключевые слова: *материалы перовскита, редукция CO_2, фотокатализ, преобразование энергии, защита окружающей среды*

Introduction. The escalating concentration of atmospheric carbon dioxide (CO_2) due to anthropogenic activities has become a pressing global concern, driving the search for sustainable technologies to mitigate its environmental impact. Specially, the transportation industry, specifically automobiles, is one of the largest contributors to atmospheric pollution, primarily through the emission of greenhouse gases like CO_2. Cars are a major source of CO_2 emissions, which are released during the combustion of fossil fuels, and these emissions significantly contribute to global warming and climate change. As global populations increase and urbanization expands, the need to mitigate the impact of car emissions on the environment has never been more pressing. Photocatalysis, particularly through the use of perovskite materials, has emerged as a promising technology for addressing this challenge. These materials, with their ability to catalyze the reduction of CO_2 into useful products, offer a potential solution to reduce the environmental impact of car emissions and other sources of atmospheric pollutants. By harnessing solar energy to drive these reactions, photocatalytic processes could play a crucial role in combating climate change and creating more sustainable energy systems. Among various strategies, photocatalytic reduction of CO_2 into value-added fuels or chemicals has emerged as a promising approach to simultaneously address energy and environmental challenges. The efficiency of such processes critically depends on the choice of photocatalyst, which must possess appropriate band structures, high surface area, and excellent charge separation capabilities. Perovskite materials, characterized by the general formula ABO_3, have attracted considerable attention in this context due to their unique structural flexibility,

tunable electronic properties, and robust physicochemical stability. Their ability to accommodate a wide variety of cations at both A- and B-sites enables precise engineering of optical and electronic features, which is crucial for enhancing light absorption and charge carrier dynamics. Moreover, the presence of oxygen vacancies and variable valence states in perovskite oxides further promotes redox activity, making them highly effective for catalytic applications. Recent studies have demonstrated that perovskite-based photocatalysts can efficiently activate CO_2 molecules, facilitate electron transfer, and selectively produce fuels such as CO, CH_4, and methanol under solar irradiation.

Perovskite Materials. The versatility of perovskite materials extends beyond single ABO_3 structures to double and layered derivatives, allowing fine-tuning of surface chemistry, charge mobility, and light-harvesting efficiency. These attributes, combined with emerging synthesis techniques such as sol-gel, co-precipitation, and 4D printing of perovskite hydrogels, have paved the way for high-performance, stable, and scalable photocatalysts. Consequently, perovskite materials stand out as a promising class of compounds for advancing CO_2 photoreduction technologies and addressing the global energy-environment nexus.

Perovskite materials, named in honor of the Russian mineralogist Lev Alekseyevich von Perovski, form a distinctive family of compounds defined by their exceptional crystal structure and versatile physicochemical properties. Their natural abundance and structural adaptability have rendered them highly attractive for applications spanning photovoltaics, optoelectronics, piezoelectric devices, and emerging technologies, including solar energy conversion, CO_2 reduction, organic pollutant degradation, energy storage, and various electronic devices [1]. Among transition metal oxides (TMOs), perovskite oxides are particularly notable for their ability to host a wide variety of cations at both the A- and B-sites of their ABO_3 lattice. Partial cation substitution at these sites introduces oxygen vacancies and variable valence states, enabling fine-tuning of structural and electronic characteristics. Remarkably, approximately 90% of elements in the periodic table can potentially occupy these positions, providing significant compositional flexibility (Fig. 1). In the idealized ABO_3 structure, A-site cations reside at the cube corners, typically represented by rare-earth or alkaline-earth metals with a coordination number of 12, while B-site cations, generally six-coordinated transition metals, occupy the unit cell center, and oxygen atoms occupy the face-centered positions. The structural robustness and compositional versatility of perovskites make them ideal candidates for electrocatalytic applications.

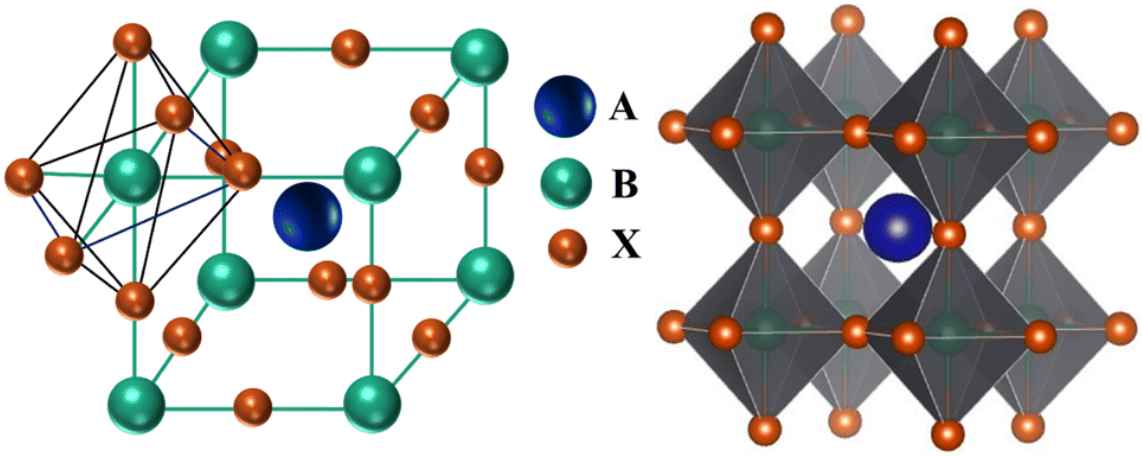


Figure 1. *The basic structure of ABX_3 with corner-sharing BX_6 octahedral [2]*

The coexistence of multiple cation species allows precise tuning of electronic and catalytic properties, thereby enhancing their performance in oxygen evolution reactions (OER) and other electrochemical processes. Specifically, their diverse redox behavior, coupled with favorable ionic

and electronic conductivities and chemical stability, contributes to their high electrocatalytic activity. Strategies to optimize the photoelectrocatalytic performance of perovskite oxides include surface deposition of noble metals, cation doping, and coupling of semiconductors with complementary band structures (e.g., Z-scheme configurations). Ion doping enables modulation of the bandgap and alteration of intrinsic crystal structures, with ions such as Li^{+}, Fe^{3+}, Mn^{2+}, Y^{3+}, $NaNbO_3$, and $KNbO_3$ being commonly employed [3–7]. Additionally, codoping at the A-site can stabilize B-site metal valences, further enhancing photocatalyst durability. Despite their versatility, perovskite oxides face limitations that can hinder electrochemical performance. High initial overpotentials during OER, low specific surface areas, and limited electrical conductivity can reduce the number of active sites and impede charge transfer. Furthermore, structural degradation or phase transitions over time can compromise long-term stability.

Perovskite derivatives also include ferroelectric compounds, which exhibit spontaneous polarization. First described by Joseph Valasek in 1920 through studies on Rochelle salt, ferroelectric materials, primarily complex oxides, are utilized in actuators, non-volatile memories, capacitors, sensors, and energy harvesters [8, 9]. Their A-sites typically accommodate alkali, alkaline-earth, or rare-earth cations, whereas B-sites host transition metals, and X-sites (O, N, etc.) complete the lattice. Rational element substitution at these sites enables precise tuning of crystal and electronic structures, thus affecting physical properties and photocatalytic performance [10]. Perovskites, including ABO_3 and A_2BO_4 oxides, demonstrate low cost, chemical stability, and multifunctionality, with applications in catalysis, adsorption, optics, magnetism, electronics, and ferroelectricity. They are employed in oxygen-permeable membranes, fuel cells, magnetic materials, sensors, and wastewater treatment. Various synthetic techniques-sol-gel, proteic, Pechini, combustion, co-precipitation, and chelating precursor methods-allow control over structural and functional properties, optimizing perovskites for specific applications [11]. Their structural resilience and ability to accommodate diverse cations make them particularly suitable for photocatalytic, electrocatalytic, and photoelectrocatalytic processes. In photocatalysis, perovskites efficiently absorb light over broad spectra, facilitating charge carrier generation for reactions such as water splitting or CO_2 reduction. In electrocatalysis, reversible redox behavior and tunable chemical composition enhance catalytic activity. In photoelectrocatalysis, the combination of light absorption and electrochemical reactivity allows efficient conversion of solar energy to chemical energy. Careful engineering of composition and structure ensures broad applicability of perovskites in sustainable energy solutions.

Classifications of perovskite materials. *Lead-based perovskites* are a distinctive class of materials that have gained attention not only in the realm of optoelectronics but also for their potential applications in photocatalysis, particularly in the reduction of CO_2. These materials are structured in the form of the perovskite crystal lattice, with lead ions occupying the B-site of the structure. The chemical flexibility of perovskite materials allows for various modifications, making them versatile for different applications, including CO_2 reduction. The unique feature of lead-based perovskites lies in their ability to absorb a wide range of the solar spectrum and generate electron-hole pairs upon light absorption. This makes them particularly promising for solar-driven photocatalytic reactions. Recent studies have focused on developing lead-based perovskites with high stability and efficiency in photocatalytic CO_2 reduction. Researchers have explored different compositions, such as the use of formamidinium and methylammonium lead halides, to optimize the photocatalytic performance. For example, lead-based perovskites like $CH_3NH_3PbI_3$ [12] have demonstrated exceptional CO_2 reduction activity under visible light. The material's high light absorption and efficient charge separation have been identified as key factors contributing to its photocatalytic performance. Moreover, the incorporation of other elements or hybridization with other materials has been explored to improve the stability and selectivity of CO_2 reduction products, such as methane and carbon monoxide. However, despite the promising performance of lead-based perovskites, the toxicity of lead and the challenges related to their stability in aqueous environments

or over prolonged use remain a critical concern. Consequently, ongoing research is focused on improving the environmental safety and long-term performance of these materials. This has led to the exploration of strategies like lead replacement, protective coatings, and the development of composite materials that combine the advantages of lead-based perovskites with those of other stable materials.

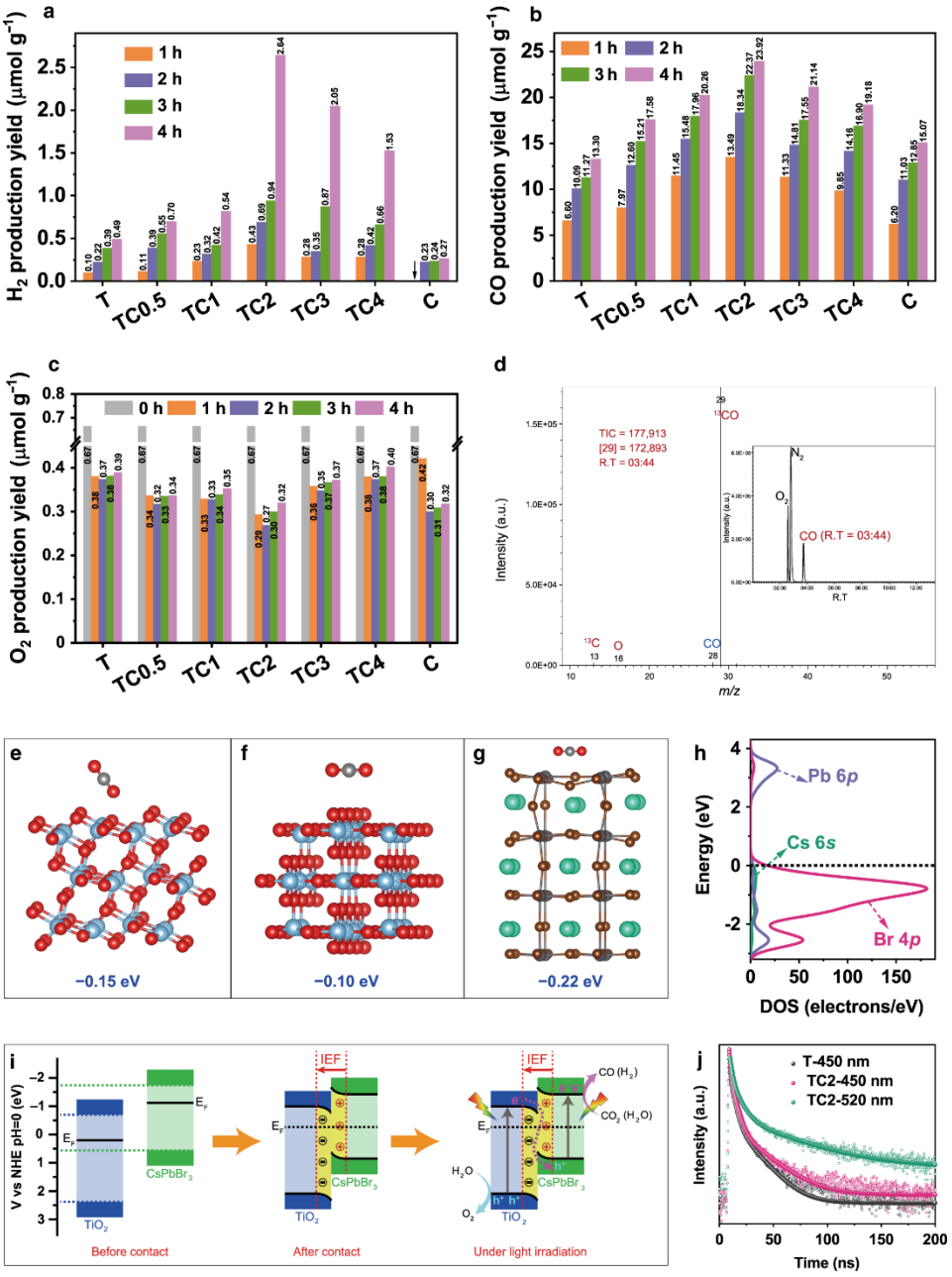


Figure 2. *Photocatalytic activities of CO_2 reduction over TiO_2, TCx, and $CsPbBr_3$ quantum dots (QDs) during 4-h experiment performed under UV–vis light irradiation: time course of (a) H_2, (b) CO, and (c) O_2 production yields. (d) Mass spectra of 13CO and total ion chromatography (inset) over TC_2 in the photocatalytic reduction of $13CO_2$. Optimized structures of CO_2 molecule adsorbed on (e) anatase TiO_2 (101), f rutile TiO_2 (110), and (g) $CsPbBr_3$ (001) facets. h The DOS of $CsPbBr_3$. (i) Schematic illustration of $TiO_2/CsPbBr_3$ heterojunction: internal electric field (IEF)-induced charge transfer, separation, and the formation of S-scheme heterojunction under UV–visible-light irradiation for CO_2 photoreduction. (j) Time-resolved photoluminescence (TRPL) spectra of TiO_2 (T) and TC_2 at emission wavelengths of 450 and 520 nm, respectively.*

In summary, lead-based perovskites represent a promising material class for photocatalytic CO_2 reduction due to their high efficiency, tunable properties, and significant progress in research aimed at addressing their limitations. These materials are an exciting area of investigation for advancing renewable energy technologies and mitigating the impacts of climate change through the conversion of CO_2 into useful products. For example, cesium lead bromide ($CsPbBr_3$) quantum dots have demonstrated significant photocatalytic activity for CO_2 reduction. When combined with graphene oxide, these composites exhibit enhanced charge separation and increased production of CO and CH_4 under visible light irradiation.

The introduction of graphene oxide facilitates electron transfer, improving overall catalytic efficiency. This approach underscores the potential of integrating perovskite quantum dots with carbon-based materials to enhance photocatalytic performance [13]. Moreover, in the study [14], authors have developed TiO_2/perovskite ($CsPbBr_3$) S-scheme heterojunctions via a straightforward electrostatic-driven self-assembly method, Fig.2. Both density functional theory (DFT) calculations and experimental observations confirm the electron transfer from $CsPbBr_3$ quantum dots (QDs) to TiO_2, leading to the formation of an internal electric field (IEF) that directs from $CsPbBr_3$ to TiO_2 upon hybridization. This IEF facilitates the movement of photoexcited electrons from TiO_2 to $CsPbBr_3$ under light irradiation, as demonstrated by in-situ X-ray photoelectron spectroscopy (XPS) analysis. The results indicate the creation of an S-scheme heterojunction within the TiO_2/$CsPbBr_3$ nanohybrids, significantly enhancing the separation of electron-hole pairs, thereby improving CO_2 photoreduction efficiency. The hybrid nanofibers exhibit a higher CO_2 reduction rate of 9.02 μmol g^{-1} h^{-1}, compared to pristine TiO_2 nanofibers, which show a rate of 4.68 μmol g^{-1} h^{-1}. Isotope ($13CO_2$) tracer experiments further validate that the reduction products are derived from the CO_2 source.

$Cs_2AgBiBr_6$, a lead-free double perovskite, has shown promising results in photocatalytic CO_2 reduction. Under visible light, this material produced CO and CH_4, demonstrating its potential as a stable and efficient photocatalyst. The stability and photocatalytic activity of $Cs_2AgBiBr_6$ make it a viable alternative to lead-based perovskites for CO_2 reduction applications [14].

In recent years, 2D materials have garnered significant attention as promising supporting materials across various applications. The combination of halide perovskites with 2D materials presents an effective strategy for enhancing charge transfer and minimizing electron-hole recombination in perovskite-based photocatalysts. In a notable study conducted by Xu et al. in 2018, the $CsPbBr_3$/Pd Schottky junction was developed to investigate the improved electron consumption rate for CO_2 photoreduction [15]. The $CsPbBr_3$ nanocrystals (NCs) were deposited onto Pd nanosheets under ambient conditions using a simple technique on a glass substrate, and the photocatalytic reduction of CO_2 to CO and CH_4 was examined. The dynamics of charge transport and carrier behavior within the composite were analyzed through photoluminescence (PL) and femtosecond transient absorption spectroscopy (fs-TAS). A notable PL quenching of 0.5–8.6% was observed in the $CsPbBr_3$/Pd composite compared to the pristine sample, as shown in Figure 3a. Similarly, the time-resolved PL (TRPL) analysis revealed a reduced PL decay with an average lifetime of 2.71–13.38 ns for the composite, compared to 52.03 ns for pure $CsPbBr_3$ (Figure 3b). A consistent trend was observed in the fs-TAS analysis, where the composite exhibited a significantly lower peak intensity compared to the pristine $CsPbBr_3$ (Figure 3c). These results suggest that the integration of $CsPbBr_3$ with Pd nanosheets reduces the recombination rate of electron-hole pairs, thereby enhancing the CO_2 reduction process to form CH_4 and CO (Figure 3d). Remarkably, the Schottky junction formed between the $CsPbBr_3$/Pd composite resulted in an increased electron consumption rate of up to 33.80 μmol g^{-1} (for CH_4 and CO production), 2.43 times higher than that of the pure $CsPbBr_3$, with improved quantum efficiency (Figure 3e, f). These findings demonstrate that combining halide perovskites with 2D materials is a promising approach for photocatalytic CO_2 reduction.

Perovskite oxides, a subclass of perovskite materials, have emerged as promising candidates for photocatalytic CO_2 reduction due to their unique crystal structure and tunable properties. These materials, characterized by the ABO_3 structure, allow for the modification of electronic properties and catalytic activity by adjusting the A- and B-site cations. Their high ionic and electronic conductivity, redox activity, and stability make them ideal for CO_2 reduction reactions. Materials like $SrTiO_3$, $LaFeO_3$, and $BaTiO_3$ have shown strong photocatalytic performance, producing carbon-based fuels like methane, carbon monoxide, and formic acid.

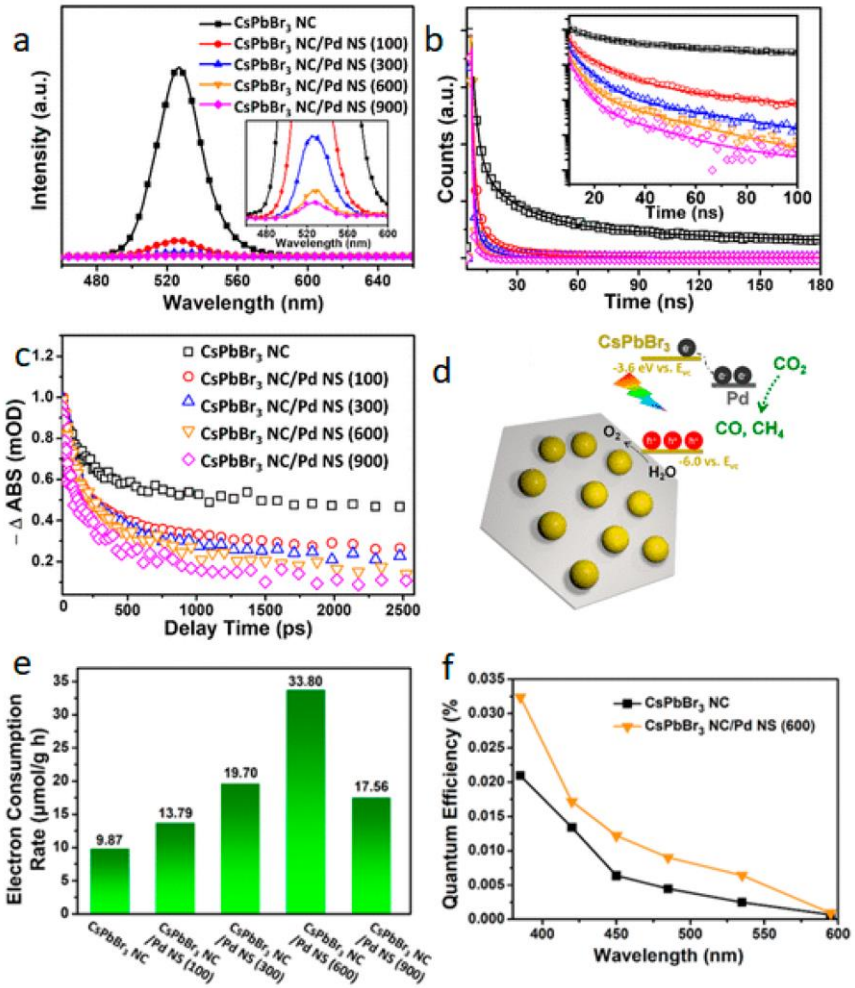
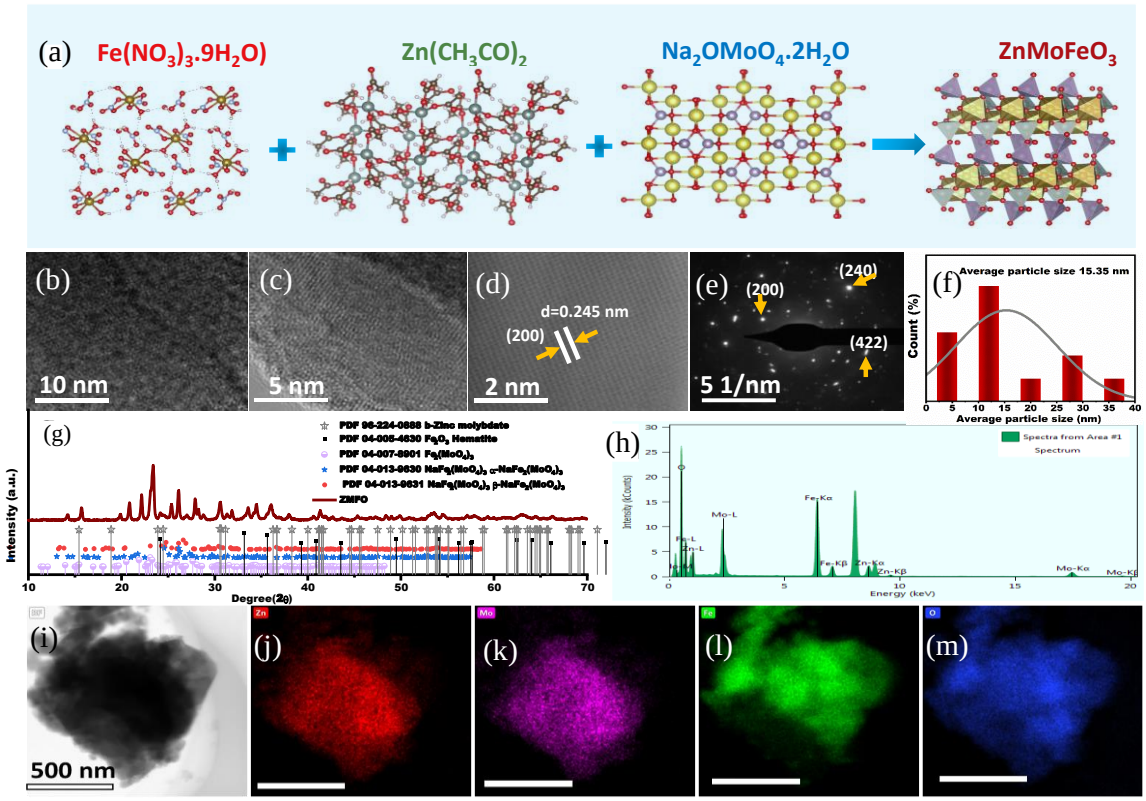


Figure 3. *The comparative (a) PL spectra, (b) PL decay, (c) transient absorption kinetic plots (at an excitation wavelength of 400 nm) among $CsPbBr_3$ NC and composite samples, (d) schematic illustration and band alignment of $CsPbBr_3$/Pd composite for CO_2 reduction, (e) photocatalytic CO_2 reduction performance, and (f) quantum efficiency of different samples.*

The metal cations at the B-site and surface modifications, such as oxygen vacancy engineering, enhance their photocatalytic efficiency. Despite promising results, challenges like stability and product selectivity remain, prompting ongoing research into optimizing these materials or combining them with other semiconductors. Perovskite oxides offer great potential for sustainable energy applications in CO_2 reduction. For example, $LaCoO_3$, a perovskite oxide, has been utilized as a cocatalyst in photocatalytic CO_2 reduction. When combined with other photocatalysts, $LaCoO_3$ enhances the production of CO under visible light irradiation. Its role as a cocatalyst underscores the importance of perovskite oxides in facilitating efficient CO_2 reduction processes [16].

Incorporation of sulfur (S) and carbon (C) into Sr_2CoTaO_6 perovskite oxide has been shown to boost its photocatalytic CO_2 reduction activity by more than eleven orders of magnitude compared to the pristine material. This enhancement is attributed to improved charge carrier dynamics and increased surface area, highlighting the significance of compositional modifications in perovskite oxides for photocatalytic applications.

Two-dimensional perovskites have garnered attention for their stability and unique excitonic properties, making them suitable for photocatalytic CO_2 reduction. These materials exhibit high stability under photocatalytic conditions and possess exciting characteristics such as quantum well structures and high exciton binding energies, which can enhance photocatalytic efficiency [men].



Figuire 4. *(a) Synthetic illustration of the optimized geometrical structure of $ZnMoFeO_3$, (b-e) HRTEM and HAADF-STEM (f) average particle size (g) XRD (h) EDS spectra (i) TEM*

Specially, novel perovskite $ZnMoFeO_3$ (ZMFO) nanosheets as promising semiconductor photocatalysts for CO_2 reduction. Experimental results show that ZMFO has a narrow bandgap, exceptional visible light response, large specific surface area, high crystallinity, and various surface-active sites, leading to an impressive photocatalytic CO_2 reduction activity of 24.87 $\mu molg^{-1}h^{-1}$ and strong stability. Theoretical calculations reveal that CO_2 conversion into CO and CH_4 on the ZMFO surface follows formaldehyde and carbine pathways. This study provides significant insights into designing innovative perovskite oxide-based photocatalysts for economical and efficient CO_2 reduction systems [1], Figure 4.

Metal-organic frameworks (MOFs) are a class of materials that consist of metal ions or clusters coordinated to organic ligands, forming a porous and crystalline structure. MOFs have gained significant attention in photocatalytic CO_2 reduction due to their high surface area, tunable porosity, and the ability to incorporate different metal centers, which can act as catalytic sites. Their

structural flexibility, along with the possibility of functionalizing the organic ligands, makes them ideal candidates for enhancing photocatalytic performance.

One notable example of MOFs in CO_2 reduction is MOF-5 (also known as IRMOF-1), which consists of zinc ions connected by terephthalic acid ligands. MOF-5 is known for its high surface area and porosity, which provides a large number of catalytic sites for CO_2 adsorption. Studies have shown that modifications to the linker molecules or the inclusion of co-catalysts, such as gold nanoparticles or copper ions, can significantly enhance its photocatalytic activity for CO_2 reduction. ZIF-8, a zinc-based MOF with imidazolate linkers, is another widely studied material for photocatalytic CO_2 reduction. ZIF-8 has a high surface area and thermal stability, which is beneficial for photocatalytic processes that require high temperatures. Its microporous structure is ideal for CO_2 capture, and doping with transition metals or coupling with other semiconductors has been shown to improve its CO_2 reduction efficiency. Additionally, MIL-101 is a chromium-based MOF with a large surface area and a flexible structure, which can accommodate various metal centers to enhance its photocatalytic activity. The incorporation of platinum or palladium nanoparticles into MIL-101 has been explored to improve its performance in CO_2 reduction reactions. In general, MOFs exhibit promising properties for photocatalytic CO_2 reduction, such as their high surface area, tunable porosity, and the ability to integrate catalytic sites. However, challenges remain in improving their efficiency, selectivity, and stability under practical reaction conditions. Continued research into the design and functionalization of MOFs, as well as their integration with other catalytic materials, is essential to overcome these challenges and make MOF-based photocatalysts viable for large-scale CO_2 reduction applications [17].

Conclusions. Perovskite materials, especially perovskite oxides and lead-based variants, exhibit significant potential in photocatalytic CO_2 reduction. Their distinctive crystal structures, capacity to incorporate a wide variety of cations, and adjustable electronic properties offer a flexible platform for enhancing photocatalytic performance. Despite notable improvements in their efficiency and durability, there are still key challenges to address, particularly regarding product selectivity, long-term stability, and the integration of these materials into large-scale applications. A primary challenge in applying perovskite materials for CO_2 reduction is optimizing product selectivity. Current systems often generate multiple by-products, and achieving higher specificity for desired products such as methane or methanol remains a significant challenge. Moreover, the durability of perovskite materials under extended use is an issue, as they are prone to degradation, which diminishes their effectiveness over time. Enhancing their resistance to environmental stressors such as light, temperature fluctuations, and humidity is crucial for their sustained application in real-world settings.

To overcome these challenges, ongoing research is focused on modifying perovskite materials through methods like doping, hybridization, or composite formation to improve both stability and selectivity. Furthermore, optimizing reaction parameters, such as utilizing co-catalysts, controlling pH levels, and improving light absorption, is essential for advancing performance. Another critical area of research is scaling up perovskite-based photocatalytic systems for practical implementation, which will require advancements in material synthesis and reactor design.

In summary, while several obstacles remain in the widespread application of perovskite materials for CO_2 reduction, continuous innovation in material modification, reaction optimization, and scaling methods promises significant advancements. These developments hold great potential for advancing sustainable energy sources and carbon-neutral technologies, making substantial contributions to mitigating climate change.

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Məqalə qəbul olunub: 14.10.25
Tövsiyə edib: prof. Həsənov Y.N.