

Review

Research Progress on Photocatalytic Reduction of CO₂ by Modified Layered Double Hydroxides

Xiaojie Zhao , Xin Xie, Yuxuan Li, Xinyi Li and Xiujuan Yu *

College of Pharmacy, Hebei North University, Zhangjiakou 075000, China

* Correspondence: yuxiujuan810@163.com

Abstract

The use of solar energy and semiconductor photocatalysts to reduce carbon dioxide (CO₂) into high-value fuels and chemicals is a promising approach to alleviate the current energy crisis and climate change. Layered double hydroxides (LDHs) are a special two-dimensional anionic clay material with a brucite-like structure. They have excellent properties such as adjustable layer cation types, interlayer anion types, and layer ratio. LDHs have been widely used in catalytic fields such as carbon dioxide reduction, water splitting, and ammonia synthesis, and are considered safe and green new photocatalysts. In recent years, researchers have conducted in-depth studies on the photocatalytic CO₂ reduction performance of hydrotalcite-like materials and have made certain progress. However, the low carrier mobility and low light utilization efficiency of pure LDHs greatly limit their catalytic reaction ability and further applications. More and more scientists are exploring methods based on regulating the structure of LDHs to improve the conversion efficiency and light utilization of products, such as changing the layer composition of LDHs, introducing vacancies in LDH structures, or coupling different types of semiconductors to construct heterojunctions. This article first summarizes the development history and structural properties of LDHs; Secondly, the mechanism of photocatalytic reduction of carbon dioxide was summarized; Thirdly, the application of LDH-based materials in photocatalytic reduction of CO₂ was classified and summarized. Although LDH-based photocatalysts have made significant progress in the field of photocatalytic reduction of CO₂, further exploration is still needed to investigate their photocatalytic active sites, mechanisms of action, synergistic mechanisms between components, and interfacial reaction mechanisms.

Keywords: layered double hydroxide; modified layered double hydroxide; CO₂; photocatalytic CO₂ reduction; catalysts



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1. Introduction

The rapid development of globalization and industrialization has not only accelerated population growth and economic development, but also greatly increased human demand for fossil fuels [1]. The huge consumption of fossil fuels not only brings about a serious energy crisis, but also emits a large amount of combustion products, among which CO₂ is the main product. The increase in CO₂ concentration in the atmosphere greatly affects the carbon cycle in nature, leading to serious environmental problems, especially the negative impact of the greenhouse effect, glacier melting, increased global rainfall and so on [2–4]. Therefore, it is necessary to explore an efficient and low-cost method for reducing carbon dioxide emissions. Among the many developed methods for converting carbon dioxide, using renewable solar energy to drive catalysts can reduce the concentration of CO₂ in the

environment and convert it into useful fuels and chemicals such as methane, methanol, formic acid, low-carbon hydrocarbons, etc. It can partially alleviate the increasingly tense energy crisis and has considerable economic benefits. It is a promising method that will have significant implications for environmental protection, rational utilization of carbon resources, and sustainable development of human society [5,6].

The key to photocatalytic CO₂ reduction technology is photocatalytic materials, which are one of the important factors determining the practical application of the photocatalytic CO₂ reduction process. Therefore, exploring and preparing various efficient photocatalytic materials is currently the main research direction in the field of photocatalysis [7]. Over the past few decades, researchers have developed various novel solar-driven photocatalytic materials, such as titanium dioxide (TiO₂)-based materials [8–11], traditional metal oxides (M_xO_y) [12,13] or metal sulfide-based (M_xS_y) semiconductor photocatalysts [14,15], bismuth-based catalytic materials [16,17], two-dimensional (2D) nanolayered materials (graphene, graphitic carbon nitride, hydrotalcite-like materials), etc. [18–20]. Among them, layered double hydroxides (LDHs), as a type of 2D nanolayered material, have garnered widespread attention in the field of photoelectrocatalysis due to their unique structural characteristics and abundant derivatives of nanocatalysts [21,22]. However, like other traditional photocatalytic materials, LDHs exhibit drawbacks such as high photogenerated electron-hole recombination rates and poor product selectivity [23]. In recent years, efforts have been made to modify LDHs, such as introducing vacancies, loading, doping, and constructing semiconductor heterojunctions [24–27], to enhance their photocatalytic CO₂ reduction activity (Figure 1).

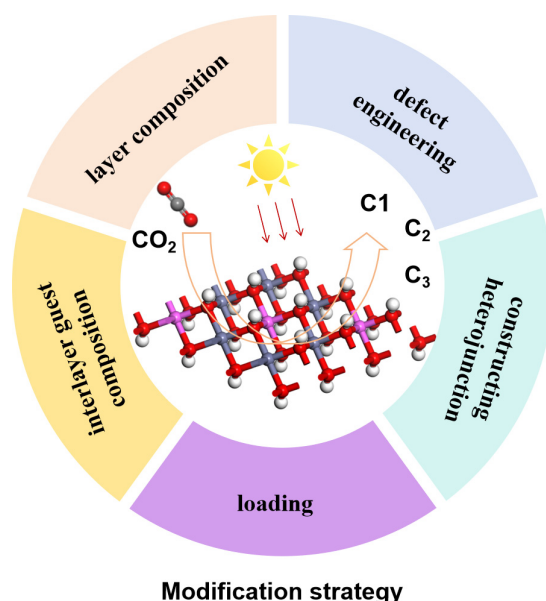


Figure 1. Schematic illustration of modification strategies for layered double hydroxides (LDHs) covered in this review.

Although several review articles on LDHs have been published, most of them have significant limitations in covering photocatalytic CO₂ reduction, especially in systematically classifying modification strategies for LDHs. This article categorizes the currently discovered LDH-based catalytic materials for photocatalytic reduction of CO₂, reviews the applications of LDH-based materials in this field, and summarizes their corresponding progress and prospects in photocatalytic reduction of CO₂, aiming to facilitate readers' understanding of the types of LDH photocatalytic materials and the design and development of novel and efficient photocatalytic materials.

2. Development History and Structural Properties of LDHs

Hydrotalcite-like materials are a unique type of two-dimensional anionic clay materials, also known as layered double hydroxides (LDHs) or anionic clay materials [28]. The discovery of layered double hydroxides can be traced back to 1842, when Swedish scientist Hochstetter first identified a white powder-like mineral resembling hydrotalcite in schist [29]. In 1942, Feitknecht et al. synthesized MgAl-LDHs in the laboratory for the first time by reacting metal salt solutions with alkali, and proposed a layered structure model, laying the foundation for artificial synthesis [30]. In 1969, Allmann et al. determined the crystal structure of MgAl-LDHs through single-crystal X-ray diffraction, clarifying its hydrotalcite-like layered characteristics [31]. In the 1970s, the Miyata team systematically studied the catalytic properties of LDHs and first used them as catalyst precursors in industrial reactions such as alkylation and transesterification, promoting the research on the chemical applications of LDHs [32]. In the 1990s, with the application of experimental techniques such as X-ray absorption spectroscopy (XAS) and high-resolution transmission electron microscopy (HRTEM), details such as the interlayer anion arrangement and charge distribution of LDHs were revealed, and their structural flexibility (such as anion exchange and interlayer spacing adjustment) was deeply understood [33,34]. Since the 21st century, the application fields of LDHs have expanded from traditional catalysis to energy (photocatalysis and electrocatalysis) [35,36], environmental remediation (pollutant adsorption) [37], biomedicine (drug delivery and tumor treatment), and other directions [38,39], becoming a cross-disciplinary research hotspot.

LDHs are compounds composed of positively charged host layers and negatively charged interlayer guests [40]. The host layers are octahedral $M(OH)_6$ structures formed by the covalent bonding of metal (M) and hydroxyl (OH) groups, which endows the LDH host layers with a positive charge. To maintain the electroneutrality of the LDH material, anions are often introduced into the interlayer space (Figure 2) [41]. Therefore, the general chemical composition formula of LDHs is $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+} \cdot (A^{n-})_{x/n} \cdot mH_2O$, where M^{2+} and M^{3+} represent divalent and trivalent cations, respectively (such as Mg^{2+} and Al^{3+} , as well as transition metal elements: Fe^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Fe^{3+} , etc.), and A^{n-} denotes interlayer anions (such as monovalent anions: NO_3^- , halide ions: X^- ; divalent anions CO_3^{2-} and SO_4^{2-} , etc.) [42]. Since the discovery and initial synthesis of LDHs, researchers have conducted in-depth studies on them. Nowadays, hydrotalcite-like materials have been widely used as photocatalysts. By utilizing the tunable composition and ratio of host layers, as well as the adjustable types and quantities of interlayer anions, the structure and electronic properties of these materials can be controlled, thereby enhancing their photocatalytic performance [43].

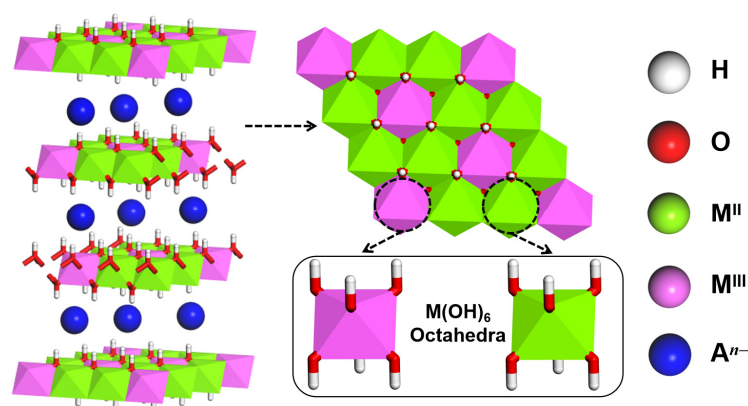


Figure 2. Ideal structural model of hydrotalcite-like materials. (M^{II} represents divalent metal cations; M^{III} represents trivalent metal cations; Aⁿ⁻ represents interlayer anions).

3. Mechanism of Photocatalytic Reduction of Carbon Dioxide

Photocatalysis refers to a light-induced photochemical process. Semiconductor photocatalysts produce photogenerated electron-hole pairs under suitable light illumination, which participate in redox conversions and reduce the apparent reaction activation energy. Photocatalytic reduction of carbon dioxide (CO₂PR) involves the excitation of electron-hole pairs in semiconductor materials under illumination, driving the multi-electron reduction reaction of CO₂ molecules to produce carbon-based fuels (such as CO, CH₄, CH₃OH, etc.). Its mechanism mainly involves multiple processes such as light absorption, carrier separation, adsorption of reactants, and surface reactions [44]. In the process of photocatalytic reduction of carbon dioxide, firstly, the semiconductor photocatalyst absorbs light with sufficient energy greater than its band gap. Electrons are excited from the valence band (VB) to the conduction band (CB), simultaneously leaving positively charged holes in the valence band. Secondly, photogenerated CB electrons and VB holes migrate toward the catalyst surface, surface-accumulated conduction band electrons act as reduction active sites, while valence band holes serve as oxidation active sites. At the reduction active sites, photogenerated electrons react with carbon dioxide molecules, undergoing a series of electron transfer and proton coupling steps, ultimately reducing carbon dioxide to methane (CH₄), formic acid (HCOOH), methanol (CH₃OH), and other substances. At the oxidation active sites, holes react with water or other electron donors to generate oxygen or other oxidation products [45]. Due to the complex multi-electron coupling proton processes involved in the reaction, different reaction pathways, C-C coupling steps, and differences in the adsorption ability of intermediates result in the diversity of CO₂PR products. The mechanism diagram of photocatalytic reduction of CO₂ to C₁ and C₂ and above is shown in Figure 3 [46]. Among them, the two-electron pathway produces CO and HCOOH, the six-electron pathway produces CH₃OH, the eight-electron pathway produces CH₄, and the pathway with 12 electrons or more produces C₂₊ products [44–46]. In photocatalytic reactions, the selectivity of products can be regulated by changing the design of the catalyst. Rational modulation of layer composition, interlayer structure, loaded nanoparticles, surface defects and heterointerfaces all adjust the adsorption strength of CO₂ intermediates and electron transfer paths, thus shifting the distribution of reduction products. Detailed analysis based on various reported LDH catalytic systems will be presented in the following sections.

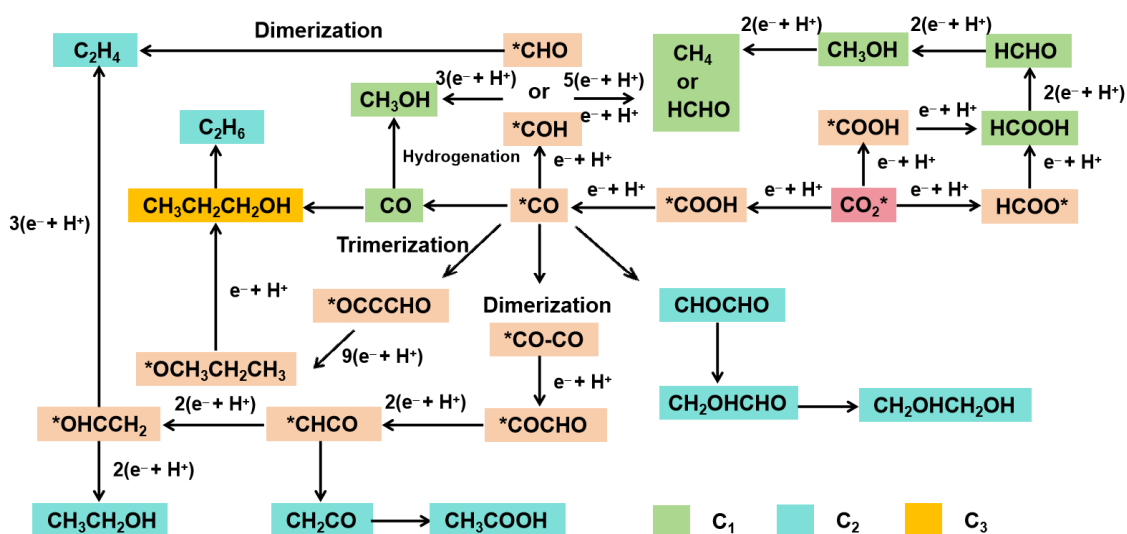


Figure 3. Schematic diagram of the mechanism of photocatalytic reduction of CO₂ to different products [46]. (* represents the catalyst surface).

4. Application of Modified LDHs in Photocatalytic Reduction of CO₂

Due to their excellent CO₂ adsorption performance, large specific surface area, and abundant active sites, LDHs have garnered increasing attention in the field of photocatalysis [47]. However, some pure LDHs exhibit high carrier recombination rates, wide band gaps, and poor visible light response, which greatly limit their practical applications [48]. Therefore, exploring suitable modification methods to enhance the catalytic activity of LDHs is of great significance for promoting their application in CO₂ photoreduction. Typically, researchers enhance the photocatalytic efficiency of LDHs and promote the selectivity of photocatalytic CO₂ reduction products by regulating the structural composition of LDHs, introducing vacancies, and constructing heterojunctions [49–51].

4.1. Regulation of Layer Composition

4.1.1. Photocatalytic Reduction Performance of CO₂ over LDHs Regulated by Bimetallic Elements

The layered composition and elemental ratio of LDHs are adjustable, allowing most elements from the periodic table to be incorporated into their layers, thereby altering their light absorption and chemical properties to achieve functionality [52]. The tunability of the metal element composition and stoichiometric ratio of metal cations in the layers is a core advantage of LDHs, directly influencing the band structure, *d*-band center position, and charge density of metal active sites, which collectively adjust the binding strength between catalyst surfaces and critical intermediates such as *COOH, *CHO and *CO. This provides important insights for the design of efficient photocatalysts for photocatalytic oxidation/reduction reactions. The regulation of LDH layer composition mainly involves bimetallic regulation and the synergistic effect of trimetallic or polymetallic systems [52].

Our research group, led by Zhao et al. [53], utilized Hubbard-corrected density functional theory to calculate the electronic properties, including band structures and electronic density of states, as well as the thermodynamic mechanism and thermodynamically favorable products of CO₂ photoreduction (CO₂PR) for ten types of M^{II}₂M^{III/IV}-LDHs (M^{II} = Mg²⁺, Co²⁺, Ni²⁺, Zn²⁺; M^{III} = Al³⁺, In³⁺, Cr³⁺, Fe³⁺; M^{IV} = Ti⁴⁺). The results revealed that for Mg₂Al-, Mg₂In-, Co₂Al-, Ni₂Ti-, Zn₂Al-, Zn₂Cr- and Zn₂Ti-NO₃-LDHs, the primary product of CO₂PR is CH₄, whereas Co₂Fe-LDH produces HCOOH. By defining an effective driving force and fitting its relationship with the adsorption energy of CO₂ and the valence band minimum (VBM) of LDHs, it was found that Mg₂In-NO₃-LDH has the highest potential for the photocatalytic reduction of CO₂ to CH₄, while Mg₂Al-NO₃-LDH has the highest potential for the photocatalytic reduction of CO₂ to CO (Figure 4).

Zhong et al. [54] prepared a series of MAI-LDHs containing different divalent metal cations (M = Mg²⁺, Ni²⁺, Cu²⁺, Zn²⁺) and tested their CO₂ conversion under solar energy. The results confirmed that the type of divalent metal cation had a significant impact on the yield of the product, with NiAl-LDHs > CuAl-LDHs > ZnAl-LDHs > MgAl-LDHs. Among them, NiAl- and CuAl-LDHs exhibited stronger light-harvesting capabilities and better charge separation performance, which is related to their enhanced adsorption and activation of CO₂ due to the shift in the *d*-band center (Figure 5).

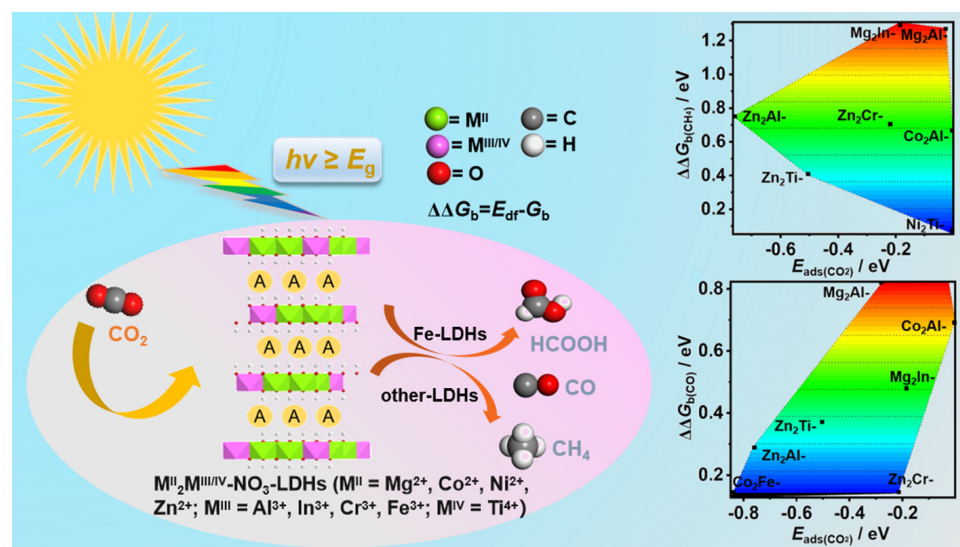


Figure 4. Photocatalytic reduction of CO₂ products on M^{II}₂M^{III/IV}-LDHs (M^{II} = Mg²⁺, Co²⁺, Ni²⁺, Zn²⁺; M^{III} = Al³⁺, In³⁺, Cr³⁺, Fe³⁺; M^{IV} = Ti⁴⁺) [53].

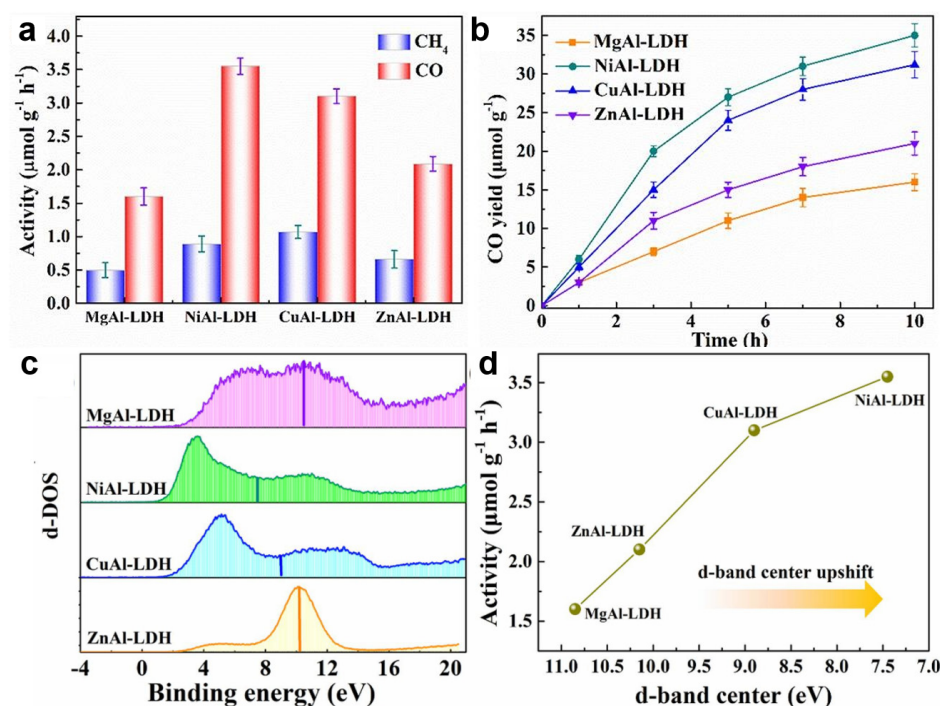


Figure 5. (a) Photocatalytic activity; (b) time-yield plots; (c) d-band center; (d) the relationship between activity and d-band center of MgAl-, NiAl-, CuAl-, and ZnAl-LDHs [54].

4.1.2. Photocatalytic Reduction Performance of CO₂ over LDHs Regulated by Three Metals Elements

The synergistic effect of tri-metal or multi-metal is similar to the doping strategy, that is, by doping appropriate elements into LDHs composed of bimetallic compounds to construct ternary or multi-component LDHs, the layer composition of LDHs can be flexibly changed to optimize the electronic structure of LDHs and enhance light absorption, thereby improving the photocatalytic performance [55]. Additionally, introducing doping elements into the LDH layer can easily introduce some defects, forming abundant coordination unsaturated sites, which can improve charge separation performance and further enhance catalytic activity [56]. Therefore, it is crucial to study the mechanism of element doping

and understand the impact of doping on the photocatalytic CO₂ reduction activity of LDH materials.

Song et al. [56] introduced Ni species into CoFe-LDH as a visible light photocatalyst, combined with a Ru complex sensitizer, enabling the highly selective reduction of CO₂ to CH₄ and CO. Compared to CoFe-LDH catalyzing CO₂ with a CH₄ yield of 0%, the selectivity for CH₄ increased to 78.9% after doping with Ni. Furthermore, under high-wavelength light irradiation ($\lambda > 500$ nm), the selectivity for the by-product H₂ could be suppressed to 1.7% (Figure 6a). Extended X-ray Absorption Fine Structure (EXAFS) confirmed the presence of oxygen and metal vacancies in NiCoFe-LDH after the introduction of Ni species. Further calculations using density functional theory (DFT) indicated that the introduction of Ni species could lower the energy band, facilitating carrier separation and thus enhancing the photocatalytic reduction performance of the material for CO₂ reduction (Figure 6b).

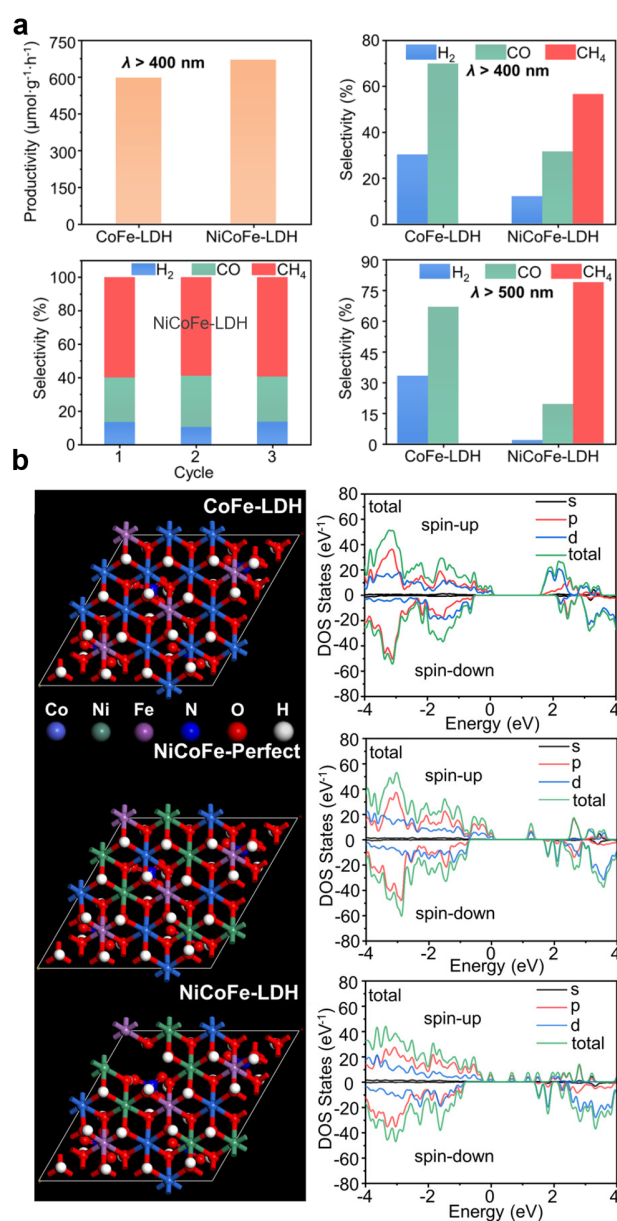


Figure 6. (a) Production rate, stability tests of selectivity and selectivity of CH₄, CO, and H₂ under $\lambda > 400$ or 500 nm for CoFe-LDH and NiCoFe-LDH; (b) structural models, DOS, and TDOS diagrams of CoFe-LDH, NiCoFe-Perfect, and NiCoFe-LDH with O and Co vacancies [56].

Zong et al. [57] constructed a series of models for non-Cu-based $M_2M'-NO_3$ -LDHs ($M = Mg, Co, Ni, Zn$; $M' = Al, Ga$), and calculated electronic properties such as band structure, density of states, work function, and band edge positions, as well as the Gibbs free energy of CO_2 reduction to different products. They found that the main products of the calculated LDHs were CO and CH_4 , with the optimal pathway being: $* + CO_2 \rightarrow CO_2^* \rightarrow OCOH^* \rightarrow CO^*/HCOOH^* \rightarrow CHO^* \rightarrow HCHO^*/HCOH^* \rightarrow CH_2OH^* \rightarrow CH_3OH^* \rightarrow CH_3^* \rightarrow CH_4^* \rightarrow * + CH_4$. Based on this, a Cu-doped model $(ZnCu)_2Ga-NO_3$ -LDH was constructed, and it was found that due to the Jahn-Teller effect of Cu, the catalyst exhibited enhanced adsorption of CH_3OH^* and reduced adsorption of CH_3^* , which in turn made the Gibbs free energy of $CH_3OH^* \rightarrow CH_3^*$ greater than 0, preventing further reduction and favoring the formation of CH_3OH , revealing the influence of Cu doping on CH_3OH selectivity (Figure 7).

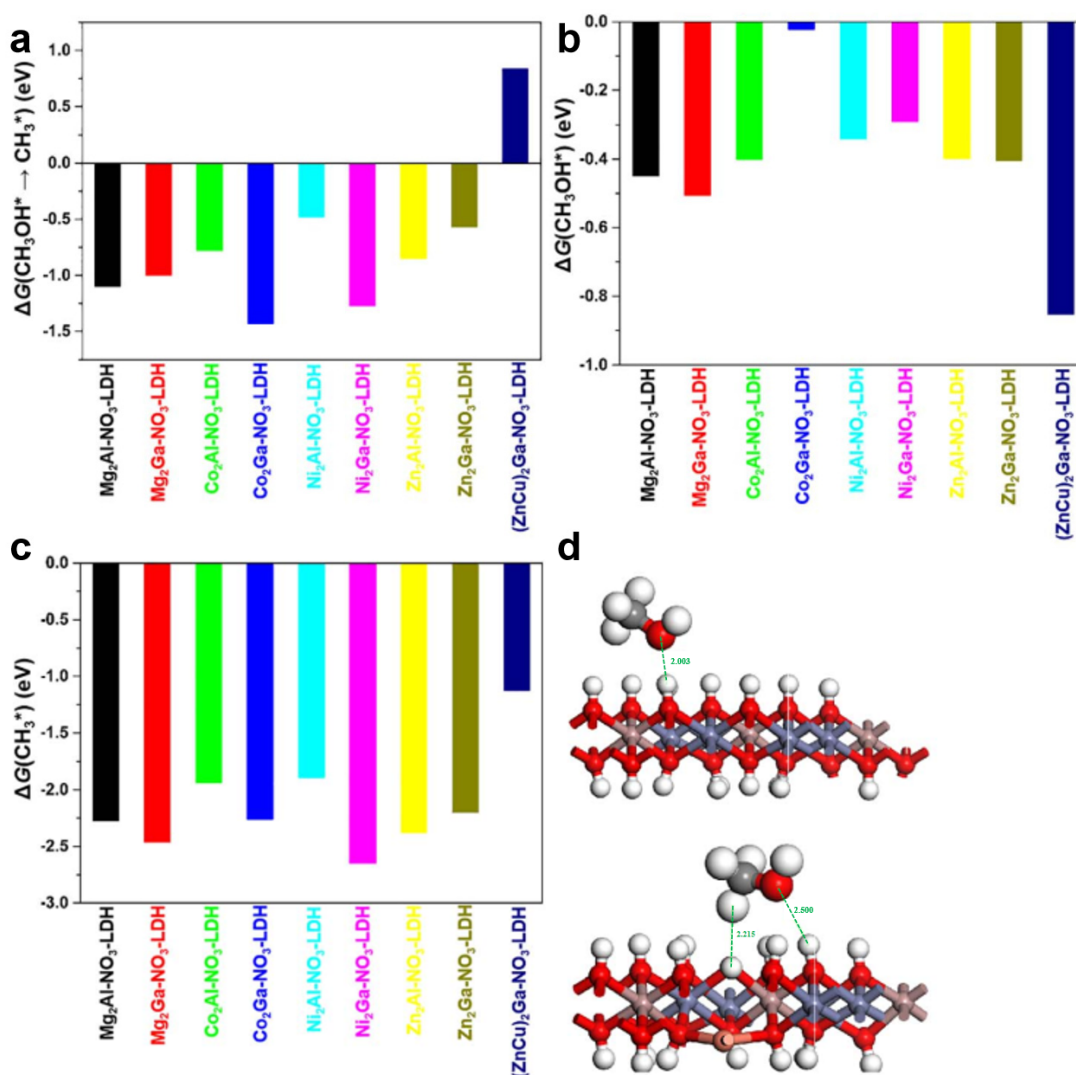


Figure 7. Gibbs free energy change for (a) the further reduction of CH_3OH^* to CH_3^* , (b) adsorption of CH_3OH^* on the catalyst, (c) adsorption of CH_3^* on the catalyst; (d) geometrically optimized structures of CH_3OH^* on the surfaces of Zn_2Ga-NO_3-LDH and $(ZnCu)_2Ga-NO_3-LDH$ [57].

4.2. Regulation of Interlayer Guest Composition

In addition to regulating the composition of metal cations in the LDH layered plates, altering the type of interlayer guest anion composition is also an effective method to enhance its catalytic activity. Due to the unique anion exchange capability of LDHs, many functional anions (such as simple inorganic anions, composite anions, and biological

macromolecules) can be introduced into the interlayer of LDHs, thereby endowing the LDH material with excellent catalytic performance [58]. Introducing different anions, molecules, or functional materials into the interlayer of LDHs can optimize the CO₂ adsorption capacity, charge transfer, and reaction kinetics of LDHs.

Song et al. [59] prepared two types of NiAl-LDH photocatalysts intercalated with NO₃[−] or CO₃^{2−} as interlayer guests, and investigated their photocatalytic reduction performance of CO₂ in the presence of electron donors and photosensitizers. The results showed that under visible light irradiation, the selectivity of Ni₂Al-NO₃-LDH (6.1%) for CH₄ was 12.2 times higher than that of Ni₂Al-CO₃-LDH (0.5%), demonstrating excellent CO₂PR catalytic performance (Figure 8). This was further confirmed to be attributed to the structural distortion of NO₃-containing LDHs, leading to more oxygen and metal vacancies, exposing more coordination-unsaturated sites, which are beneficial for carrier separation. Simultaneously, Ni₂Al-NO₃-LDH exhibited higher absorptivity and excellent charge transfer performance in the visible light region, effectively generating CH₄.

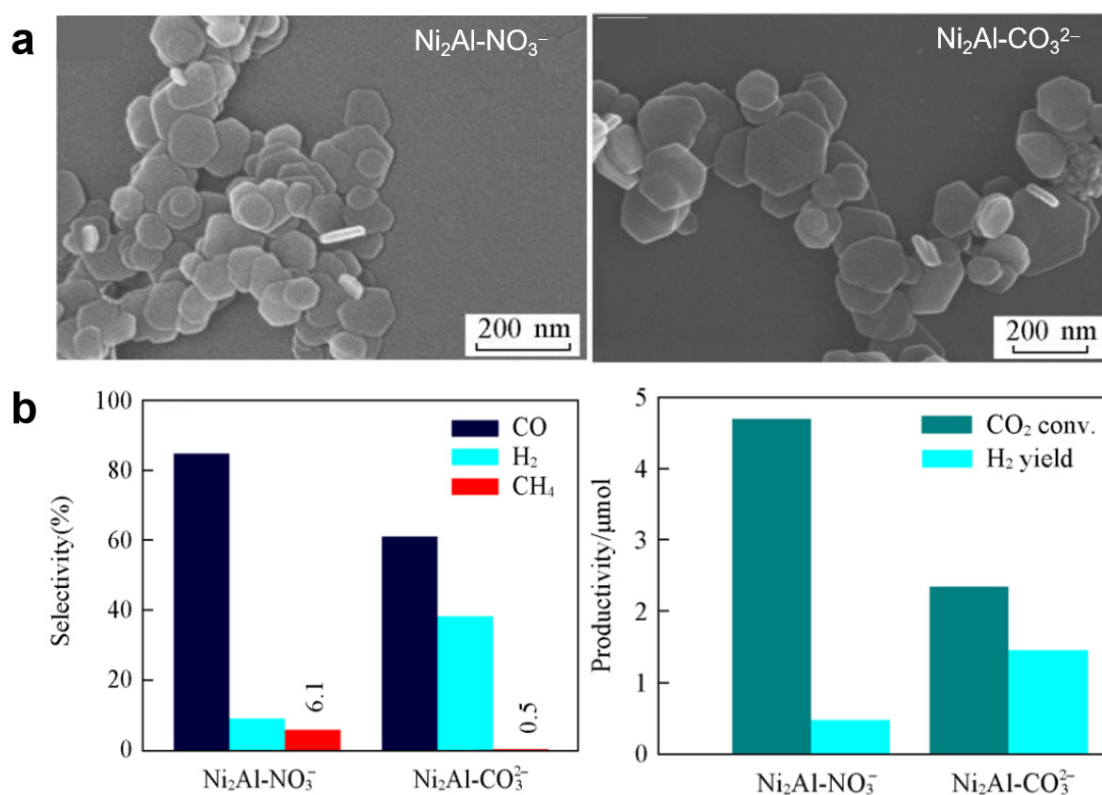


Figure 8. (a) SEM images of Ni₂Al-NO₃[−] and Ni₂Al-CO₃^{2−}; (b) product selectivity, CO₂ conversion rate, and H₂ yield of Ni₂Al-LDH with different anions [59].

Lu et al. [60] introduced organic small molecules, 4,4'-diaminostilbene-2,2'-disulfonic acid (DAS) and 4,4'-dinitrostilbene-2,2'-disulfonic acid (DNS), into the interlayer of Ni₂Mn-LDHs through co-precipitation in situ oxidation method. Compared to the original Ni₂Mn-LDHs-CO₃, the catalytic effect of Ni₂Mn-DAS and DNS-*n* (*n* = 10:0, 8:2, 5:5, 2:8, 0:10) was significantly improved. Due to the π - π interaction between DAS and DNS occurring in the interlayer, it facilitated the transfer of DAS- and DNS-photogenerated electrons to LDHs, thereby participating in CO₂ reduction (Figure 9a,b). This work provides a new approach to enhance the CO₂ photoreduction activity of hydrotalcite-based photocatalysts through the combination of organic small molecules and inorganic semiconductors.

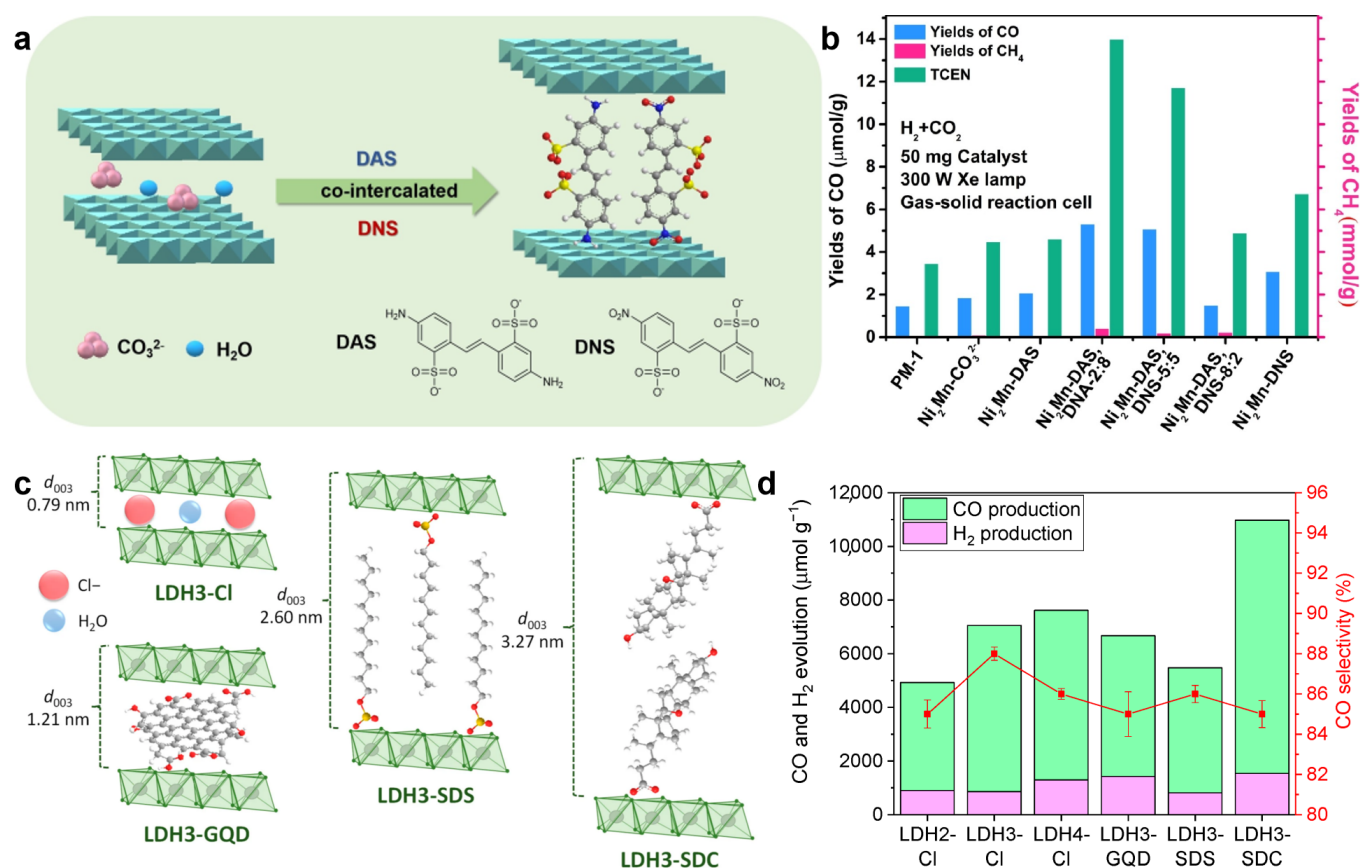


Figure 9. (a) Schematic diagram of the structure of $\text{Ni}_2\text{Mn-DAS}$, DNS-n , and (b) the yield of CO and CH_4 under UV-vis for different types of catalysts [60]; (c) schematic diagram of different interlayer anion arrangements in Zn-Cr-LDHs, and (d) the evolution of CO/ H_2 and CO selectivity after 24 h of reaction [61].

Romero-Salguero et al. [61] prepared ZnCr-LDH materials with different interlayer anions and different layer plate ratios of chloride ions (Cl^-), graphene quantum dots (GQDs), sodium dodecyl sulfate (SDS), and sodium deoxycholate (SDC) through the co-precipitation method. The prepared materials were characterized by different instrumental techniques, and their photocatalytic performance for CO_2 reduction was evaluated under visible light ($\lambda = 450 \text{ nm}$). The results showed that all the LDH materials exhibited good photocatalytic activity for CO generation. Among them, LDH3-SDC exhibited the best catalytic performance, achieving a CO selectivity of 88% after 24 h of visible light irradiation (Figure 9c,d).

Zhao et al. [62] addressed the issue of insufficient utilization of infrared light (NIR) in the photocatalytic CO_2 reduction (CO_2PR) process by intercalating an anionic Ru complex between NiAl layered double hydroxide (LDH) nanosheets, successfully constructing a NiAl-Ru-LDH photocatalyst (Figure 10). DFT calculations showed that the intercalated material could absorb 1200 nm infrared light and promote the CO_2 reduction process.

4.3. Loading

The use of supported LDHs as photocatalysts for CO_2 reduction has garnered increasing attention from scientists. Typically, metals, metal compounds, and non-metallic materials are dispersed on the layer of LDHs, exploiting the synergistic effect between the two components to broaden the light response range of photocatalytic materials, enhance the transmission efficiency of photogenerated carriers, and further facilitate the occurrence of photocatalytic reactions.

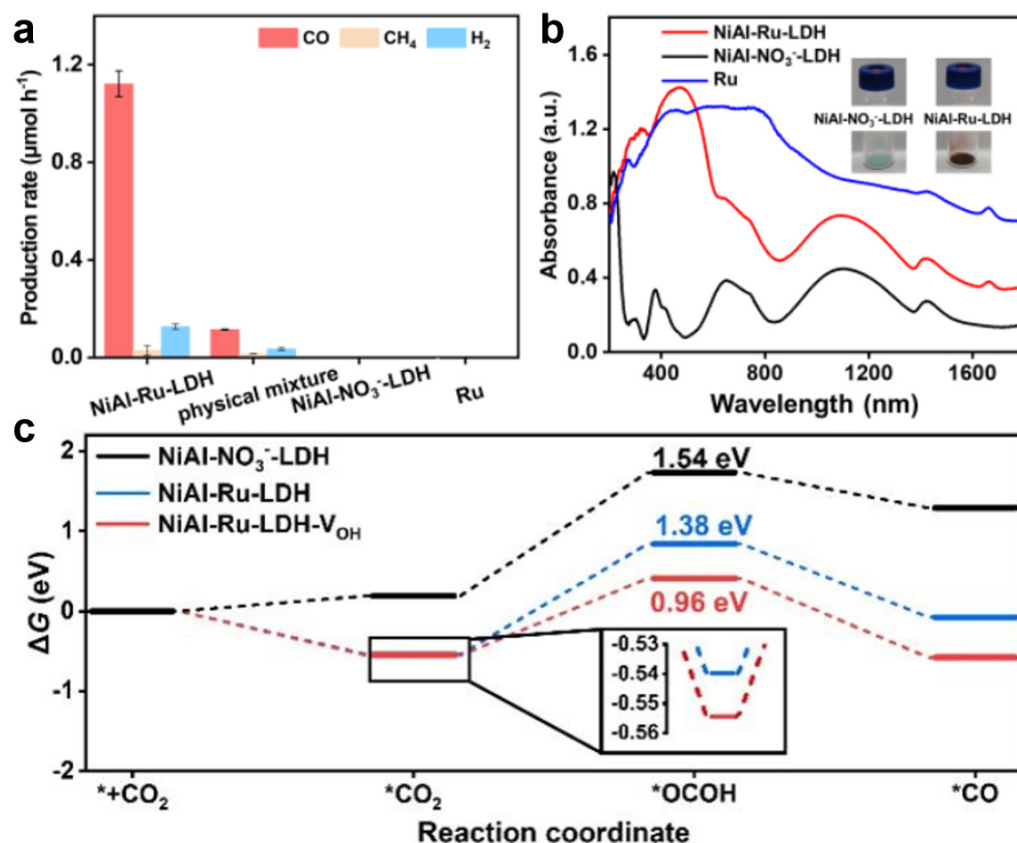


Figure 10. (a) Yield in CO₂PR under visible-NIR irradiation above 400 nm; (b) UV-Vis-NIR spectra; (c) energy profiles for CO₂PR catalyzed by different LDHs [62].

Song et al. [63] reported that in the photocatalytic CO₂ reduction reaction, with the incorporation of Ru-complex sensitizers, as the Pd content in Pd/CoAl-x increased from 0, 0.55 wt%, 5.46 wt% to 7.57 wt%, the CO generation rate decreased from 2.03, 1.68, 1.18 to 0.58 mmol·g⁻¹·h⁻¹, respectively. The H₂ generation rate changed from 1.50, 1.78, 1.59 to 1.30 mmol·g⁻¹·h⁻¹, respectively, thus achieving regulation of the CO/H₂ ratio in the products (Figure 11). Synthesis gas could still be obtained under light irradiation with $\lambda > 600$ nm. Density functional theory calculations indicated that the loading of palladium not only improved charge transfer efficiency but also promoted the formation of more H atoms into H₂, thereby adjusting the CO/H₂ ratio in the products.

Okada et al. [64] prepared a series of Pt, Pd, and Au-loaded Zn-Cr LDHs and evaluated their photocatalytic reduction of CO₂. The results showed that all the samples exhibited photocatalytic performance under ultraviolet irradiation, capable of converting CO₂ into CO. Among them, the LDH loaded with 0.1% Pt demonstrated the highest performance (Figure 12). It was proposed that this was attributed to the noble metal acting as a co-catalyst, not only reducing the recombination of electrons and holes but also enhancing multi-electron reduction reactions.

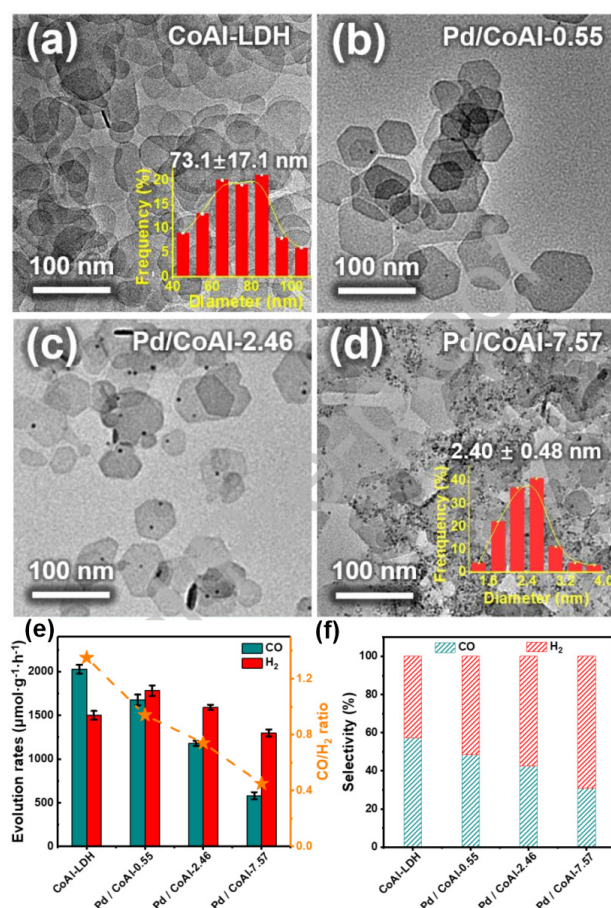


Figure 11. TEM images of (a) CoAl-LDH, (b) Pd/CoAl-0.55, (c) Pd/CoAl-2.46, (d) Pd/CoAl-7.57; the evolution rates and ratio (e), selectivities (f) of CO and H₂ on Pd/CoAl-LDHs under visible light irradiation [63].

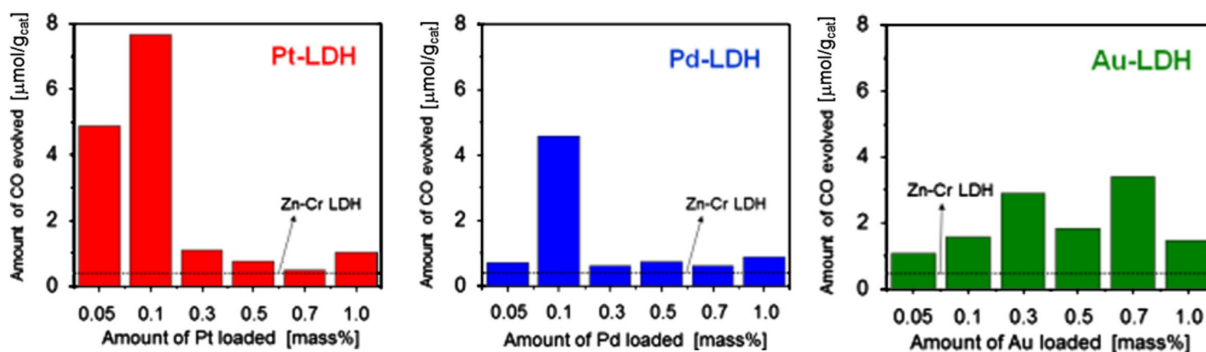


Figure 12. CO production from CO₂ photocatalytic conversion on Pt-LDH, Pd-LDH, and Au-LDH samples after 3 h of UV irradiation [64].

4.4. Defect Engineering

An important structural feature of LDH materials is the uniform distribution of M^{2+} and M^{3+} cations within the layered plates, while the diversity and tunability of the layered units endow them with a wide range of adjustable band gaps. Defect engineering enables fine-tuning of the structure of LDHs and regulation of their electronic structure [65]. In recent years, the introduction of defects into the LDH structure has played a crucial role in enhancing CO₂ chemisorption and facilitating electron transfer for CO₂ activation, garnering widespread attention and discussion in the field of photocatalysis.

Feng et al. [66] proposed a photocatalytic coupling process of CO₂ reduction and 5-hydroxymethylfurfural (5-HMF) oxidation mediated by LDH anionic compounds. ZnNiFe LDH was prepared by the co-precipitation method, and CO₂ was stored in the interlayer of LDHs in the form of carbonate. By selectively etching Zn²⁺, a certain amount of metal vacancy ions are introduced into LDH nanosheets, and the concentration of vacancy defects is precisely controlled by changing the etching time. Compared with unetched ZnNiFe LDHs, the CO and 2,5-furfural (DFF) yields of LDHs etched for 3 h under UV–visible light irradiation increased by 2.84 and 2.82 times, respectively. Finally, the catalytic effect of metal vacancy defects and surface hydroxyl groups was verified, and the mechanism of photocatalytic coupling was revealed (Figure 13a).

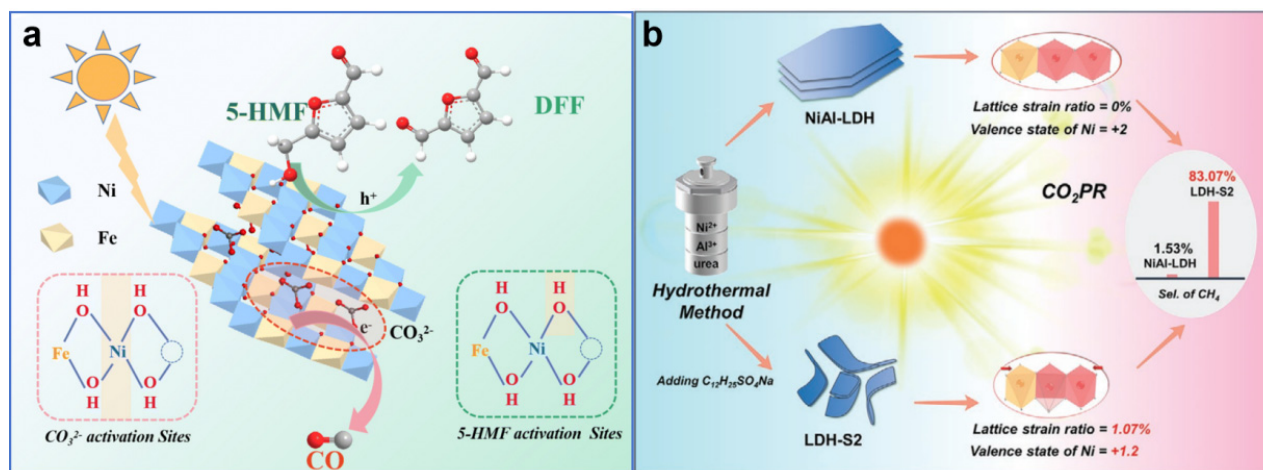


Figure 13. (a) Mechanism of the integration of CO₂ photoreduction and 5-HMF oxidation [66]; (b) schematic diagram of the preparation of NiAl-LDH and LDH-Sx, as well as their corresponding CO₂PR performance under $\lambda > 600$ nm irradiation [67].

Song et al. [67] reported the preparation of NiAl-layered double hydroxides (NiAl-LDH) embedded with surfactants (C₁₁H₂₃COONa, C₁₂H₂₅SO₄Na, C₁₆H₃₃SO₄Na), resulting in the formation of bent LDH-S1 (S1 = C₁₁H₂₃COO[−]), LDH-S2 (S2 = C₁₂H₂₅SO₄[−]), and LDH-S3 (S3 = C₁₆H₃₃SO₄[−]). Compared to NiAl LDH, LDH-S2 exhibits higher CH₄ selectivity (83.07%) and lower HER activity (3.84%) in the CO₂ photoreduction reaction (CO₂PR). Detailed characterization and DFT calculations indicate that the coupling effect between lattice deformation and electronic structure caused by V_{Ni/Al} defects in LDH-S2 enhances the activity and selectivity of CO₂PR (Figure 13b).

4.5. Constructing Heterojunction

LDHs have the characteristics of a layered structure, high porosity, and easy synthesis, and have good application prospects in the field of photocatalytic carbon dioxide reduction. However, due to the low light utilization efficiency, high carrier recombination rate, and poor recyclability of LDHs, they face more challenges in photocatalytic carbon dioxide reduction [51]. Heterojunctions have the advantages of promoting the separation of photo-generated charge carriers, suppressing photogenerated charge carrier recombination, and enhancing light absorption. Therefore, forming heterojunction structures of LDHs with other semiconductor materials to optimize their photocatalytic performance is considered a promising strategy, and many significant results have been achieved [51].

The structures of LDH-based heterostructured materials mainly include type II and type Z heterogeneous structures, which have applications in the field of photocatalytic reduction of CO₂. Pan et al. [68] synthesized a novel spherical flower-shaped In₂S₃/NiAl LDH heterojunction for the first time through a one-step hydrothermal method, and

found that it exhibited excellent photocatalytic performance and stability in the CO_2 reduction reaction under simulated sunlight irradiation. The experimental results showed that the 30% $\text{In}_2\text{S}_3/\text{NiAl}$ LDH heterojunction photocatalyst exhibited the best photocatalytic performance. Under 7 h of visible light irradiation, the maximum yield of CH_4 is $36.1 \mu\text{mol}/(\text{h} \cdot \text{gcat})$, which is approximately 2.5 times and 3.5 times that of pure LDH and In_2S_3 . The enhanced photocatalytic performance of the 30% $\text{In}_2\text{S}_3/\text{NiAl}$ -LDH catalyst is due to its efficient separation of photogenerated electron-hole pairs, which has a larger specific surface area and stronger visible light absorption ability (Figure 14a).

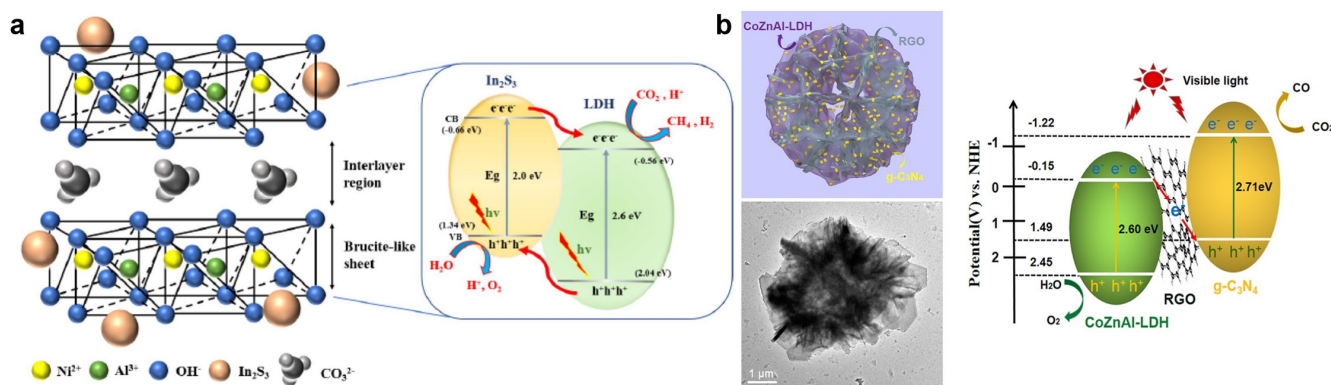


Figure 14. (a) Structure of $\text{In}_2\text{S}_3/\text{LDH}$ composite material and its photocatalytic reduction mechanism of CO_2 [68]; (b) schematic diagram of the structure and possible photocatalytic mechanism of $\text{LDH}/\text{RGO}/\text{CN}$ [69].

Zou et al. [69] synthesized CoZnAl-LDH by the hydrothermal method and loaded RGO and $\text{g-C}_3\text{N}_4$ in situ, ultimately preparing $\text{LDH}/\text{RGO}/\text{CN}$ photocatalysts with unique sea urchin-like structures. And under visible light irradiation, $\text{CoZnAl-LDH}/\text{RGO}/\text{g-C}_3\text{N}_4$ can effectively adsorb and activate reactant CO_2 and exhibit excellent selectivity towards product CO (Figure 14b).

Table 1 summarizes the activity of various modified LDH photocatalysts in photocatalytic reduction of CO_2 to different products such as CO and CH_4 . These data indicate that LDH-based materials are a very promising class of catalysts for photocatalytic CO_2 reduction. In the near future, with the development of experimental characterization technology and computer technology, more catalysts with high efficiency in reducing CO_2 will emerge.

Table 1. Summary of representative research on modified LDHs for photocatalytic CO₂ reduction.

Catalyst System	Synthesized Method	Modification Strategy	Main CO ₂ RR Products	Yield Rate (μmol·g ⁻¹ ·h ⁻¹)	Ref. No.
M-MgAl-LDH (M ²⁺ = Co ²⁺ , Ni ²⁺ , Cu ²⁺ ; M ³⁺ = Fe ³⁺ , Cr ³⁺)	Hydrothermal	Regulation of layer composition	CO	Co-MgAl-LDH (6.06) Ni-MgAl-LDH (5.47) Cu-MgAl-LDH (2.74) Fe-MgAl-LDH (3.04) Cr-MgAl-LDH (3.91)	[70]
CuMgM-LDH (M = Al, Fe)	Co-precipitation		CH ₃ COOH HCOOH CH ₃ CH ₂ OH		[71]
Ni ₇₅ Al _{25-x} Y _x -LDH	Condensation reflux		CH ₄		[72]
ZnM-LDH (M = Ti, Fe, Co, Ga, Al)	Hydrothermal		CH ₄ (ZnTi-LDH) CO (ZnAl-LDH) CO (ZnGa-LDH)	ZnTi-LDH (CH ₄ :1.2) ZnAl-LDH (CO:1.3) ZnGa-LDH (CO:1.6)	[73]
NiAl-CO ₃ -LDH NiAl-NO ₃ -LDH	Hydrothermal	Regulation of interlayer guest composition	CO, CH ₄		[59]
Au-NiAl-LDH	Ligand-mediated self-assembly	Loading	CO	2.77	[74]
CDs/NiAl-LDH@In ₂ O ₃	Hydrothermal		CO, CH ₄	CO (7.12) CH ₄ (10.67)	[75]
Pd/CoAl-LDH	Co-precipitation		CO	2.03	[63]
NiAl-LDH	Hydrothermal		CO, CH ₄	CO (712) CH ₄ (168)	[76]
CoAlLa-LDH	Co-precipitation-assisted hydrothermal	Defect engineering	CO, CH ₄	CO (21.80) CH ₄ (25.5)	[77]
NiAl-LDH/Bi ₂ Sn ₂ O ₇ -Ov/ CuO-Ov	Hydrothermal		CO, CH ₄ , C ₂ H ₆	CO (29.95) CH ₄ (18.46) C ₂ H ₆ (32.13)	[78]
CoAl-LDH	Co-precipitation		CO	1349.2	[79]
ZnAl-LDH/Bi ₂₄ O ₃₁ Br ₁₀	Electrostatic self-assembly	Constructing heterojunction	CO	84.95	[80]
NiCoMn-LDH/kaolinite	Microwave-assisted hydrothermal		CO	235	[81]
NiCo-LDH/CN-Cv	Hydrothermal		CO	39.86	[82]
Cu _{2-x} S/g-C ₃ N ₄ /NiAl-LDH	Hydrothermal		CO, CH ₄	CO (4.47) CH ₄ (28.13)	[83]
ZnFe-LDH/CuWO ₄	Hydrothermal		CO, CH ₄	CO (42.3) CH ₄ (65.17)	[84]

5. Conclusions and Prospects

LDHs have shown great potential in the field of photocatalytic reduction of CO₂ due to their low cost, easy availability, tunable structure, and unique chemical properties. This article is based on previous research and introduces the latest research progress in photo-driven CO₂ catalytic conversion in recent years from three aspects: the structure of LDHs, the mechanism of photocatalytic reduction of carbon dioxide, and modified LDHs as photocatalysts. The focus is on the regulation of LDHs' layer composition, interlayer guest composition regulation, element loading, defect engineering, heterostructure construction, etc., as catalysts to optimize the catalytic reduction performance of CO₂. Despite substantial progress in tuning the composition, defects, interlayer structure and heterostructure of LDH photocatalysts, several core obstacles still hinder their further development toward practical solar CO₂ conversion: narrow visible-light response range, severe photogenerated carrier recombination, low selectivity toward high-value C₂+ hydrocarbons and poor long-term photostability under continuous irradiation. To address these limitations, multiple promising research directions deserve sustained attention in the coming years.

(1) It is necessary to further explore precise atomic structure control strategies, including controllable construction of single-atom active sites within the LDH layer, precise regulation of oxygen/metal defect concentrations, and rational optimization of LDH electronic properties such as band structure. The interface engineering between LDHs and photosensitizers, as well as narrow-bandgap semiconductors, will still be the mainstream method for improving charge separation efficiency. Experimental characterization techniques should be closely integrated with theoretical calculations to capture short-lived CO₂PR intermediates and elucidate catalytic mechanisms.

(2) Artificial intelligence (AI) and machine learning (ML) will become revolutionary tools for breaking through the limitations of traditional LDH material trial-and-error experimental research. ML models can establish quantitative correlations between LDH composition, interlayer anion types, defect concentrations, heterojunction interfaces, and photocatalytic activity as well as CO₂PR selectivity, avoiding a large number of trial-and-error experiments; Combining ML prediction with DFT theoretical simulation can accurately calculate the adsorption energy of key CO₂PR intermediates and screen LDH systems with good reaction energy barriers, especially for the selective production of CH₃OH, C₂H₄ and other C₂+ products that are difficult to obtain through traditional modification methods. At present, the application of ML in LDH photocatalytic CO₂ reduction is still in its infancy; Establishing an open LDH experimental data sharing database and developing specialized prediction models will be an important research trend in the next stage.

(3) Other valuable research directions include the green synthesis of ultra-thin LDH nanosheets, the manufacture of integrated photocatalytic reactors loaded with LDH thin films, and the combination of LDH-based CO₂ photoreduction and biomass waste oxidation to achieve the full utilization of photogenerated carriers and maximize the redox capacity. Ultimately, the combined advancement of precise structural modification, in situ mechanism characterization, and AI-assisted material design will make the modified LDH photocatalysts closer to actual solar fuel production.

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