Review

Layered Double Hydroxide (LDH) Based Photocatalysts: An Outstanding Strategy for Efficient Photocatalytic CO₂ Conversion

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Abstract: CO₂ conversion to solar fuels/chemicals is an alluring approach for narrowing critical issues of global warming, environmental pollution, and climate change, caused by excess atmospheric CO₂ concentration. Amongst various CO₂ conversion strategies, photocatalytic CO₂ conversion (PCC) is considered as a promising approach, which utilizes inexpensive sunlight and water with a photocatalyst material. Hence, development of an efficient and a stable photocatalyst is an essential activity for the respective scientific community to upscale the PCC research domain. Until today, metal oxides, such as TiO₂, ZnO, etc., are categorized as standard photocatalysts because of their relative stability, abundant availability and low cost. However, their performance is tethered by limited light absorption and somewhat physical properties. Recently, layered double hydroxides (LDHs) have offered an exciting and efficient way for PCC due to their superb CO₂ adsorption and moderate photocatalytic properties. The LDH based photocatalysts show marvelous physiochemical and electrical properties like high surface area, stability, and excellent conductivity. In the present review article, a summarized survey is portrayed regarding latest development for LDH based photocatalysts with a focus on synthesis strategies employing various photocatalyst materials, influencing parameters and possible mechanism involved in PCC to useful fuels and chemicals like CO, CH₄, CH₃OH, and H₂.

Keywords: layered double hydroxide; photocatalytic CO₂ conversion; surface modifications; composite nanostructures; CO₂ conversion mechanism

1. Introduction

Ever increasing energy demand for rapid industrialization/urbanization, being fulfilled mainly from fossil fuels, is continuously stimulating the alarming and severe threats of environmental pollution and global warming [1]. It is believed that amongst various global house gases (GHG), increased atmospheric CO₂ gas concentration contributes to the major portion for the respective critical issue [2–4]. Industrialization and utilization of fossil fuels are considered as the prime driving factors for excessive CO₂ levels. Therefore, in accordance with the adverse sentiment, it is imperative to adopt and promote an alternative technology that provides an efficient, renewable, and sustainable pathway to counterbalance excessive atmospheric CO₂ level. In this regard, photocatalytic CO₂ conversion (PCC) or photo-reduction to useful/value added chemicals (CO, CH₄, C₂H₆, C₂H₅OH, C₂H₄, CH₃OH, HCOOH, etc.) is one of the most engaging and alluring approaches. PCC is based on the concept of natural photosynthesis, employing a semiconductor material acting as a photocatalyst with a

reducing agent (e.g., $\text{H}_2\text{O}/\text{H}_2$ etc.) for CO_2 conversion to useful chemicals under the light irradiation, a free energy source [5–7]. Generally, PCC is considered as a research domain under the umbrella of artificial photosynthesis, targeting normalization of CO_2 level and providing chemicals/fuels in a sustainable manner.

Since the pioneering work of Inoue et al., the photocatalysis field has been researched extensively with respect to materials [8]. As well-established, titanium dioxide (TiO_2) is counted on as one of the best photocatalytic materials due to its specific characteristics of abundant availability, high stability, better charge lifetime, favorable surface area, non-toxicity, and cost effectiveness [9]. However, despite certain benefits, TiO_2 also possesses the major drawback of a limited light absorption due to its wide band gap and limited CO_2 surface adsorption. Until now, enormous efforts and researches have been done to achieve an efficient photocatalytic CO_2 conversion on the account of process development, such as materials with broadened light absorption, higher surface area, enhanced CO_2 adsorption, and photocatalytic reactors advancement [10–14]. For the case of photocatalytic materials development, certain strategies have been executed such as doping [15,16], composite/hybrid/heterojunction formation [17–21], nano-architectures [22–24], and coupling with noble metals or carbon-based materials [22,25,26]. All such approaches are oriented towards attaining outstanding photocatalytic CO_2 conversion efficiency.

Recently, layered double hydroxide (LDH), an interesting class of layered anionic clays, has captivated the researchers' interest for their development and application in a variety of research domains such as adsorption [27], photocatalysis [28], electrochemistry [29–32], and biomedical science [33]. Generally, LDHs are synthetically produced and rarely occur in nature. The exceptional properties of LDH, i.e., their superb adsorption capacity extended light absorption via compositional variation, cheap synthesis procedure, and unique layered morphology, making them suitable materials for photocatalysis applications [28]. Until now, a moderate number of researches and studies have been reported employing LDH regarding their synthesis approaches and electronic and physical properties influencing photocatalytic applications [32,34]. However, specific to PCC, there exist limited reports employing bare LDH, surface modified LDH, or hybrid LDH based photocatalysts.

In the present review, the recent progress of bare LDH and LDH based photocatalysts employed for photocatalytic CO_2 conversion to useful chemicals/fuels are briefly overviewed. The synthesis procedure involved, key reaction conditions, PCC mechanism, and prime parameters promoting the improvement of photocatalytic performance are detailed. In short, the review is a brief overview of LDH based photocatalysts offering excellent performance for PCC.

2. Layered Double Hydroxide (LDH) Structure and Synthesis

LDH are mainly synthetic materials with their structure mimicking natural mineral hydrotalcite ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot \text{H}_2\text{O}$) was discovered in 1842 and synthetically prepared in 1942 [35]. The detailed structural investigation of the LDH was conducted by Allmann and co-authors in 1969 [36]. Hence, LDH are composed of layered structure and are also termed hydrotalcite-like compounds comprising brucite like metal hydroxide layers and water molecules balanced by interlayer anions. The commonly accepted formula representing the LDH is $[\text{M}_{1-x}^{2+}\text{M}_x^{3+}(\text{OH})_2]^{A^{n-}}[\text{A}^{n-}]_{x/n} \cdot m\text{H}_2\text{O}$, where M^{2+} (e.g., Mg^{2+} , Cu^{2+} , Ni^{2+} , Zn^{2+} etc.) and M^{3+} (e.g., Al^{3+} , Fe^{3+} , Ga^{3+} etc.) represents the divalent and trivalent cations, respectively. A^{n-} indicates the interlayer gallery ions such as CO_3^{2-} , NO_3^{2-} , Cl^- , etc. along with water molecules. The illustration of commonly acknowledged and endorsed LDH is shown in Figure 1.

It is well established that the composition of the LDH, their structure, and certain properties can be controlled and manipulated by the nature of the synthesis procedure. Primarily the synthesis procedure can be classified based on the phase involved, i.e., (1) solid phase and (2) liquid phase synthesis approach. Solid state synthesis approach mainly consists of mechanochemical process employing wet and dry milling methods [37,38]. Such approach offers benefit of less pollution in terms of liquids used but again is an expensive method, with a major drawback of structure distortion and nonuniform LDH structure. On the contrary, liquid phase synthesis approach is a commonly adopted

and dominant strategy because of its easiness, cost effectiveness, and provision of the prime benefits of complete and uniform LDH structural morphology. The liquid phase synthesis approach is further branched into variety of synthesis methods based on the reaction type [39–41]. Some of important and commonly practiced liquid phase synthesis methods can be listed as follows:

- I. Co-precipitation method;
- II. Anion exchange method;
- III. Reconstruction/rehydration method;
- IV. Solution mixing method.

Figure 1. Structural illustration of layered double hydroxide (LDH).

Amongst the above-mentioned methods, co-precipitation method is the most frequently adopted synthesis approach offering a direct method for the synthesis of LDH. Co-precipitation method practices slow addition of anionic solution to the divalent or trivalent metal cations solution, with addition of alkali or urea, resulting in hydrolysis and finally precipitation of LDH. The addition of base or urea in metal cations solution leads to co-precipitation of metallic salts via condensation of hexa-aqua metal complexes finally resulting in brucite-like metal cations layers with solvated interlamellar anions.

Anion exchange method employs the exchange of the intercalated anions by other targeted anions. In this method, already prepared LDH is subjected to stirring in the targeted anions solution, which are to be intercalated to achieve the required LDH. Moreover, when the co-precipitation method is not feasible, anion exchange method is utilized, e.g., when either metal cations or anions are unstable in alkaline solution or when there is chance of direct reaction between the cations and intercalated anions. Under these specific circumstances, anion exchange method offers viable alternative approach to synthesize the desired LDH by exchanging the intercalated anions with the target anions.

Another interesting synthesis method is the reconstruction method. Like shape memory materials, LDH materials also tend to return to their original structure. Generally, when the LDH materials are calcined at higher temperatures (400–500 °C), the intercalated anions and water molecules are completely erased, and hydroxides are converted to respective metal oxides. These metal oxides are immersed in water or targeted anion solution, and the metal hydroxide and intercalated layers of anions are regenerated, and LDH is reformed. Such process is very fruitful for intercalating the specific targeted anions in the interlayer gallery of the LDH.

Simple solution mixing and then subjecting it to high temperature and pressure conditions such as hydrothermal or solvothermal approaches are another effective mean to fabricate the LDH and/or LDH based composites with other semiconductor materials.

In addition to the abovementioned methods, i.e., hydrothermal [42], there exist a variety of synthesis methods such as sol-gel [43], and microemulsion methods [44], which can be adopted based on the required features and properties of the LDH.

3. Bare and Modified Layered Double Hydroxide (LDH) Photocatalysts

Layered double hydroxide (LDH) is mainly comprised of layered morphology, providing important aspects of (i) broader light absorption (generally in the visible light range) and (ii) better CO₂ sorption capability because of their layered morphology. Moreover, the choice of metal cations within LDH can well tune the photocatalytic activity by influencing its light absorption and sorption attributes. Ahmed et al. [45] studied the effect of the metal cation for zinc-copper-M (III) LDH, where M stands for aluminum (Al) or gallium (Ga) metal. It was observed that samples composed of ternary metal ions, i.e., ZnCuAl and ZnCuGa LDH, show a red shift in their light absorption as compared to ZnAl and ZnGa LDHs. Hence, the insertion of Cu in both mentioned LDHs extends their absorption towards the visible range, which might be due to the generation of an electronic state induced by Cu ions, thus narrowing down the band gap. Under the UV-Vis photo irradiation and reactant mixture consisting of CO₂ and H₂, the ZnCuAl and ZnCuGa LDH produced mainly CH₃OH as a key product component as compared to ZnAl and ZnGa LDHs, which mainly yielded CO as a key product. Hence, the selectivity of the product mainly from CO switches to CH₃OH with the incorporation of the Cu in the LDH. The role of Cu addition is responsible for increased production of CH₃OH as compared to CO. Cu sites within the LDH might be providing a binding site for CO₂, thus interacting with photogenerated electrons, protons, and probably the Cu^I/Cu^{II} redox couple. The proposed mechanism is shown in Figure 2a, where the interlayer hydroxyl group linked with Ga/Al and Cu ties with the CO₂ molecule resulting in hydrogen carbonate, which undergoes a series of reduction reactions in presence of protons finally forming the CH₃OH as a major product. Furthermore, the insertion of Cu narrows down the band gap and well, aligning it with the redox level of CO₂/CH₃OH as shown by energy level diagram in Figure 2b. Such a band gap alignment is favorable for producing CH₃OH under light irradiation.

As investigated in their previous research [45], the interlayer space within LDH layers acts as an active site for the CO₂ conversion to CH₃OH with higher selectivity when Cu is inserted. Hence, extending their investigation with the modification of the interlayer space of the LDH for enhancing the photocatalytic performance via anionic species between the cationic LDH layers, Ahmed and co-authors [46] found an increased CH₃OH formation rate. They found, during the synthesis process of Zn₃Ga[CO₃] and Zn_{1.5}Cu_{1.5}Ga[CO₃] LDH, the (CO₃)^{2−} is replaced with [Cu(OH)₄]^{2−} anions by [CuCl₄]^{2−} ions hydrolyzed in the alkaline solution. It was observed with the intercalation of the [Cu(OH)₄]^{2−} anions that the light absorption is shifted towards the lower energy as compared to samples with (CO₃)^{2−} anions. Moreover, Cu insertion also exhibits the absorption in the visible range due to intrinsic property of Cu ions. The Zn₃Ga[Cu(OH)₄] LDH photocatalyst exhibits 5.9 times higher CH₃OH production as compared to Zn₃Ga[CO₃] and similar to that of Zn_{1.5}Cu_{1.5}Ga[CO₃]. However, Zn_{1.5}Cu_{1.5}Ga[Cu(OH)₄] shows an increase selectivity of CH₃OH up to 88%. The investigation concludes that the modification of the respective LDH photocatalysts with the Cu(OH)₄ anions instead of CO₃ anions leads to increase of interlayer space between the LDH thus resulting in more reactive space. Secondly, the insertion of the Cu ions narrows the bandgap of the resulting LDH photocatalyst with more light absorption and thus better photocatalytic performance.

Another report investigates the role of the precursor anions for hydroxide sheets, for various LDH photocatalysts including Ni-Al, Zn-Al, Mg-In, and Ni-In [47]. The LDH were synthesized by both nitrates (LDH-NO₃[−]) and chlorides (LDH-Cl[−]) and evaluated for their photocatalytic activity in terms of CO₂ conversion to useful chemicals. It was observed that the LDH with Ni/Al ratio of 4

and synthesized using chlorides exhibited the maximum CO₂ conversion to CO. It was noticed that except Ni-Al LDH-Cl[−], all other samples selectively generate H₂; however, Ni-Al LDH-Cl[−] mainly yielded CO from CO₂ photo-reduction. The production rate of various products obtained from variety of LDH photocatalysts can be seen in Figure 3a. The reason for the selective formation of CO for Ni-Al LDH-Cl[−] can be attributed to the co-catalytic behavior of the Ni species, which in turn leads to the enhancement of CO formation as the Ni ratio is increased. For the other LDH photocatalysts, H₂ is mainly produced due to competition of H⁺ being reduced during the CO₂ photo-reduction, a well-known competitive reaction phenomenon. Furthermore, when the Ni content is decreased within Ni-Al LDH-Cl[−], the CO formation is decreased, and H₂ formation is increased, which endorses Ni species to act as a co-catalyst during the CO₂ photo-reduction reaction. The Ni-Al LDH-NO₃[−], on the contrary, showed the production of CH₄ when employed for CO₂ photo-reduction. The authors also found that Cl[−] ions in the aqueous solution also act as hole scavengers, thus promoting the selective formation of CO instead of other products.

Figure 2. (a) Photocatalytic reactions proposed for the CO₂ photo-reduction to CH₃OH employing ZnCuGa LDH. (b) Band gap alignment of ZnCuAl LDH (with varied Zn, Cu and Al ratio) against the redox potential of CH₃OH, CO and H₂. (taken with permission from reference [45]. Copyright 2011, Elsevier).

Figure 3. (a) Photocatalytic CO₂ conversion to useful chemicals over various M-Al or M-In LDH, where M stands for Mg, Ni, Zn. (b) Photocatalytic CO evolution rate and its selectivity for Ni-Al LDH with various salt additives (Figures taken with permission from reference [47] copyright 2011, Elsevier and [48] copyright 2015, The royal society of chemistry).

Continuing the role of Cl[−] ions, Iguchi et al. researched the effect of Cl[−] ions as a hole scavenger in CO₂ photo-reduction employing Ni-Al LDH [48]. Various additives were added in the aqueous solution containing suspended LDH photocatalyst, bubbled with CO₂ gas, and irradiated using 400 W high pressure mercury lamp. The additives were NaHCO₃, Na₂CO₃, Na₂SO₄, NaNO₃, and NaCl. It was observed that NaHCO₃ and Na₂CO₃ exhibited a greater selectivity towards H₂ generation due to favorable reduction of H⁺ ions generated in water. The Na₂SO₄ and NaNO₃ did not contribute in the formation of either product, H₂ or CO. However, when NaCl was used as an additive, a significant amount of CO was produced with higher selectivity as compared to all other additives. The selectivity along with production rate of H₂ and CO with various inorganic additives can be viewed in Figure 3b (dark bar represents CO, grey bar H₂ and circle represents selectivity towards CO formation). In order to understand the mechanism involved, DPD (N, N-dimethyl-p-phenylenediamine) test was performed. The DPD test indicated that when the NaCl was added to aqueous solution, the product was consisted of CO, H₂ and HClO under photoirradiation as a reaction amongst CO₂, H⁺ and Cl[−]. Hence, the formation of HClO as an oxidant product during the photoreaction indicates that Cl[−] is expected to be a strong reducing agent and is rapidly oxidized by holes in the solution leading to yield HClO and selective formation of CO.

Another report investigated the role of fluorinated surface of LDH photocatalysts and their role in the CO₂ conversion enhancement [49]. The authors fabricated fluorinated Mg-Al and Ni-Al LDH photocatalysts and evaluated their photocatalytic performance for the CO₂ conversions in aqueous solution. The fluorination was done by incorporating hexafluoroaluminate (AlF₆^{3−}) units within the hydroxide sheets of the LDH. In addition, various samples of LDH were prepared by changing the concentration of fluorine precursor, with the optimized sample providing the maximum yield of CO as a main product of CO₂ photo-reduction. It was observed and confirmed in authors previous works that the Ni-Al LDH is more efficient in selective formation of CO as compared to Mg-Al LDH as Ni species are supposed to act as co-catalyst, thus suppressing the formation of H₂. However, the optimized fluorine content (which was estimated by ratio of fluorine precursor to the aluminum precursor of LDH and was found 7.5) significantly enhances the formation of CO with NaCl as an additive for the hole scavenger. Such an improvement is mainly associated with the increased surface area of the fluorinated LDH, which leads to higher sites for CO₂ adsorption and thus increased CO₂ photo-reduction to CO.

The work done by Flores et al. investigates the role of various Mg sources, organic precursor and a one-step microwave-hydrothermal method on the photocatalytic activity of Mg-Al LDH [50]. Two different salts of magnesium, i.e., magnesium acetate and magnesium nitrate, were used with organic urea as a source of CO₃^{2−} and OH[−] within LDH layers. The LDH photocatalysts were then subjected for two different times for microwave radiation for 20 and 40 min and at a temperature of 100 °C. All the samples were employed for photocatalytic CO₂ conversion in gas as well as liquid

phase reactions. It was observed that the crystallinity of the synthesized LDH was significantly influenced by the nature of the Mg precursor and microwave irradiation time. The greater microwave irradiation time leads to formation of a larger crystallite size along with decomposition of organic urea resulting in formation of NH_4^+ , OH^- , H^+ , and CO_3^{2-} ions, which will readily react with Mg^{2+} due to higher dipole moment, thus resulting in better crystallinity. When the prepared LDH photocatalysts were employed in liquid phase for CO_2 conversion, the key product formed was CH_3OH with the highest yield obtained from Mg-Al LDH prepared by respective acetate salt under 40 min microwave radiation. Hence, by increasing the microwave irradiation time, the crystallite size and crystallinity are improved, which leads to decreased impedance, whereas, the decomposition of acetate anions adsorbed on LDH surface in turn facilitated the electron transfer towards the CO_2 sites within LDH. Such decomposition for LDH obtained by nitrates salts resulted in formation of NO_3^- , which can occupy the CO_2 active site. Figure 4a displays the CH_3OH production by various LDH photocatalysts prepared in the reported work. When the optimized LDH photocatalysts were employed for gas phase reactions, the key products obtained were CO and CH_4 . Such formation of CO and CH_4 under gas phase is more favorable due to its potential lowering than the CH_3OH formation and deoxygenation of C-species with electrons. The band gap alignment of all the Mg-Al LDH prepared in the respective work is shown in Figure 4b.

Figure 4. (a) Photocatalytic CO_2 conversion to CH_3OH for Mg-Al LDH photocatalyst; A represents acetate precursor, and N stands for nitrate precursor; 20 and 40 stands for microwave radiation time in minutes. (b) Band gap alignment of respective Mg-Al LDH against the redox potential of CH_3OH , CO, CH_4 , and H_2O . (Figures taken with permission from reference [50] Copyright 2018, Elsevier)).

A recent work done by Wang et al. presents synthesis of Co-Al LDH nanosheets for the conversion of very low concentration atmospheric CO_2 and water to CH_4 [51]. Furthermore, the investigation also focuses on the importance of alkaline OH group and divalent cobalt for efficient CO_2 conversion to CH_4 . Figure 5a,b show the morphology of the prepared Co-Al LDH nanosheets, showing hexagonal sheet like morphology and thickness of 18 nm. The unique attribute was the uniform composition of Co, Al, and O elements. The UV-Vis absorption spectrum for the Co-Al LDH nanosheets suggests the light absorption of the synthesized photocatalyst lies in the visible range with an estimated band gap of 2.1 eV. Thus, the respective photocatalyst can capture the visible range of the light, which can probably lead to improve photocatalytic performance. The synthesized Co-Al LDH nanosheets were found to be active for 55 h of irradiation with atmospheric CO_2 (400 ppm), yielding CH_4 as a main product with rate of $4.3 \mu\text{mol g}^{-1} \text{h}^{-1}$, which is 13 times higher as compared to standard TiO_2 sample, i.e., P25. The improved CH_4 generation was mainly attributed to the enhanced CO_2 adsorption by surface OH groups and unique effect of divalent cobalt. The divalent characteristic of cobalt was investigated by oxidation of the Co-Al LDH in oxygen atmosphere, and it was observed that the photocatalytic performance was sharply decreased when the LDH was oxidized. Moreover, the LDH photocatalyst exhibited a stable photocatalytic performance over five cycles of repeated reaction as

shown in Figure 5c. The mechanistic view displaying the proposed reduction mechanism for CO₂ conversion upon the surface of Co-Al LDH is shown in Figure 5d. The CO₂ reduction is proposed to initiate with the chemisorption of CO₂ and OH groups, which can bend linear CO₂ molecule, thus activating them to form carbonate species. These carbonate species in the presence of electrons and protons undergo multistep proton assisted reaction forming CO, which is finally converted to CH₄ and other useful chemicals.

Figure 5. (a,b) TEM images of the Co-Al LDH Nanosheets displaying a hexagonal type morphology. (c) Photocatalytic CO₂ conversion to CH₄ for Co-Al LDH photocatalyst over more than 5 cycles of evaluation. (d) Mechanistic view of the photocatalytic process occurring at the surface of the Co-Al LDH. (Figures taken with permission from reference [51]. Copyright 2018, The Royal Society of Chemistry).

In another work, Tokudome et al. reported synthesis of nanocrystalline Ni-Al LDH (20 nm) by simple homogenous supersaturation process induced via rapid increase of pH from concentrated aqueous salt solutions of precursors [52]. When Ni-Al LDH was employed for CO₂ conversion in aqueous medium, the CO formation rate (selectivity of 80%) was found 7 times higher as compared to the standard Ni-Al LDH prepared by conventional method. The key for the improved photocatalytic performance was attributed to the metastable surface of the nano LDH due to high degree of supersaturation. Figure 6a shows the morphology of the nano LDH and standard LDH. Nano LDH mainly consists of 20 nm particle size in agglomerated form whereas the conventional LDH is mainly composed of various size ranges of platelets within a range of 40–200 nm. Figure 6b shows the photocatalytic CO₂ conversion to CO in aqueous media. It was observed that nano LDH exhibited a significant increase in CO production as compared to standard LDH. This was mainly attributed to the surface affinity of the nano LDH towards the CO₂ adsorption in gaseous phase. Such a specific surface nature is induced mainly due to synthesis process designed in the research work. Furthermore, for the

purpose of comparison, various control samples were synthesized in order to investigate the role of morphology and crystallinity of nano LDH for CO₂ conversion. However, it was observed that all those parameters, when improved, exhibited a decrease in photocatalytic performance; hence ultimately, the metastable surface of the nano LDH and its superb affinity towards CO₂ adsorption can only be considered as the key to success of improved photocatalytic performance.

Figure 6. (a) Surface morphology of the nano Ni-Al LDH and bulk Ni-Al LDH with its surface area and particle size. (b) Photocatalytic CO₂ conversion to CO and H₂ for nano Ni-Al LDH (NLDH) and bulk Ni-Al LDH (reference LDH) with respective selectivity (Figures taken with permission from reference [52]. Copyrights 2018, The Royal Society of Chemistry).

A recently published research work by Gao et al. presented an ultrathin Mg-Al LDH modified with Fe₃O₄ by a simple coprecipitation approach [53]. It was observed that Fe₃O₄/Mg-Al LDH (FMAL) exhibited significant improvement in the photocatalytic activity, which was due to synergetic effect of efficient separation of electron-hole pairs and reduction of resistance for charges transmission induced by Fe₃O₄ and ultrathin Mg-Al LDH, respectively. Figure 7a shows the transmission electron microscopy (TEM) image of Fe₃O₄/Mg-Al LDH, which exhibits thin 2D nanosheets of Mg-Al LDH with Fe₃O₄ nanoparticles loaded on nanosheets. The UV-Vis DRS for the Fe₃O₄/Mg-Al LDH is shown in Figure 7b. The light absorption spectrum covers visible region due to presence of Fe₃O₄ nanoparticles, which possess a narrow band gap and almost act like a conductor. Such conductive behavior leads to inhibition of photogenerated electron-hole recombination, thus contributing to improved photocatalytic performance. Figure 7c,d show the photocatalytic production of CO and CH₄ by various Fe₃O₄/Mg-Al LDH samples (with varied content of Fe₃O₄). It was observed that the sample FMAL-10 with 10 wt.% of Fe₃O₄, exhibited the highest CO and CH₄ yield, and hence, it was selected

as an optimized sample. The key factors as explained above were supposed to be the efficient charge separation by the Fe_3O_4 content and the rapid transformation of the photoexcited charges towards the reactive sites on $\text{Fe}_3\text{O}_4/\text{Mg-Al LDH}$ surface. Further increase of Fe_3O_4 content decreased the light transmission characteristic and hence reduced photocatalytic performance.

Figure 7. (a) Surface morphology of the $\text{Fe}_3\text{O}_4/\text{Mg-Al LDH}$. (b) UV-Vis DRS for $\text{Fe}_3\text{O}_4/\text{Mg-Al LDH}$, Mg-Al LDH and Fe_3O_4 . (c,d) Photocatalytic CO_2 conversion to CO and CH_4 , respectively, for various $\text{Fe}_3\text{O}_4/\text{Mg-Al LDH}$, represented by FMAL with varied amount of Fe_3O_4 (Figures taken with permission from reference [53]. Copyright 2019, Elsevier).

Recently, Bai et al. reported four different types of ultrathin MAI-LDH photocatalysts (u-MAI-LDH, where M stands for Mg^{2+} , Ni^{2+} , Co^{2+} and Zn^{2+}) for CO_2 conversion to mainly CO [54]. The synthesized u-MAI-LDH were tested under visible light irradiation ($\lambda = 400\text{--}800\text{ nm}$) and employed with a $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ photosensitizer for photocatalytic CO_2 conversion to CO. Amongst various samples synthesized, the u-CoAl-LDH showed the highest efficiency, Figure 8a shows the schematic view of proposed photocatalytic CO_2 conversion employing u-CoAl-LDH with production of CO and H_2 when irradiated with visible light (400–800 nm) and light at 600 nm wavelength. Figure 8b shows that the photocatalytic reactions were not initiated without $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ and triethanolamine, thus endorsing the important roles of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ as a photosensitizer and triethanolamine as a hole scavenger for regeneration of LDH photocatalysts valence bands. Figure 8c illustrates the photocatalytic CO_2 conversion products for all the synthesized u-MAI-LDH photocatalysts. It could be observed that all samples exhibit less amount of CO and H_2 production as than u-CoAl-LDH, which exhibited the highest conversion rate. The u-NiAl-LDH sample also exhibited production of

CH₄ due to well-known selectivity of Ni towards CH₄. The key reason for improved photocatalytic performance can be associated to (i) defects on the photocatalyst surface due to its ultrathin nature thus promoting the CO₂ adsorption; (ii) improved light absorption, thus capturing the maximum of visible light region; and (iii) well matched energy levels of u-CoAl-LDH with [Ru(bpy)₃]Cl₂·6H₂O photosensitizer, thus on light irradiation the photogenerated charges are drained towards the LDH surface where they can efficiently react with the adsorbed CO₂.

Figure 8. Photocatalytic CO₂ conversion to CO, CH₄, and H₂ over (a) ultrathin CoAl-LDH, (b) under various conditions, and (c) with different ultrathin LDH photocatalysts. (Figures taken with permission from reference [54]. Copyrights 2020, American chemical society).

Another work proposed by Xiong et al. presented the role of trivalent and tetravalent in Zn based LDH photocatalysts employed for photocatalytic CO₂ conversion [55]. It was observed that choice of trivalent or tetravalent cation in the LDH photocatalyst alters the selectivity of the product. Authors synthesized a variety of ZnM-LDH (where M = Ti⁴⁺, Fe³⁺, Co³⁺, Ga³⁺, Al³⁺) and observed that ZnTi-LDH generates CH₄ as main product, whereas ZnFe-LDH and ZnCo-LDH were unable to reduce CO₂ and yield H₂ by water splitting only. Moreover, ZnGa-LDH and ZnAl-LDH yielded CO as main product of CO₂ photo-reduction. By help of in situ diffuse reflection, infrared Fourier transform spectroscopy (DRIFT), and computational calculations, it was revealed that the metal cations with d

band level (ϵ_d) closer to the fermi level interact favorably with CO_2 , leading to its well adsorption, and hence, light irradiation converts the adsorbed CO_2 into carbon containing products, i.e., CH_4 and CO , whereas the metals with d band level far from the fermi level exhibited very less CO_2 adsorption, thus yielding H_2 due to water splitting. Figure 9a shows the mechanistic view of the synthesized ZnM-LDH photocatalysts and their selectivity to certain products. Figure 9b shows the photocatalytic product generated by the ZnM-LDH photocatalysts, and Figure 9c exhibits the respective selectivity.

Figure 9. (a) Mechanistic view of various products obtained from different Zn based LDH (ZnM-LDH, where M = Ti, Fe, Co, Ga, Al) photocatalysts. (b) Photocatalytic CO_2 conversion to useful chemicals. (c) Selectivity for various ZnM-LDH photocatalysts. (Figures taken with permission from reference [55]. Copyright 2020, Elsevier).

In addition to the development of LDH photocatalysts, another important and beneficial approach is to use the LDH as a base material to convert it into a highly efficient photocatalyst. Recently, Wang et al. fabricated thin and defective $\text{NiO}/\text{Al}_2\text{O}_3$ composite from NiAl-LDH [56]. The NiAl-LDH photocatalyst was transformed to NiO with Ni and oxygen vacancies under oxidation and was investigated at various oxidation temperatures from 200–800 °C. The schematic view of the proposed mechanism for synthesis methodology is exhibited in Figure 10a. The photocatalytic CO_2 conversion to various products with selectivity can be seen in Figure 10b,c, respectively. It could be observed, NiO sample synthesized at a temperature of 275 °C, yielded maximum CH_4 under the irradiation of 600 nm wavelength light. Hence, this temperature meant to be an optimum condition for having the best oxygen and nickel vacancies.

The summary of the various bare/pure LDH photocatalysts regarding their research objective, reaction conditions, products yielded, and influential parameters are tabulated in Table 1.

Table 1. Summary of various pure/bare LDH photocatalysts with research objective, reaction conditions, value added chemicals production by photocatalytic CO₂ conversion, and key parameters for improved performance.

LDH Photocatalysts	Research Objective	Light Source and Reactants Employed	Photocatalytic Activity, CO ₂ Conversion to Value Added Chemicals	Parameters Contributing towards Improved Performance	Ref
ZnCuGa LDH and ZnCuAl LDH	<ul style="list-style-type: none"> Development of UV-Visible light active LDH with tailoring the product selectivity via Zn and Cu sites 	<ul style="list-style-type: none"> UV-visible light obtained from 500 W Xenon arc lamp CO₂ with H₂ gas were used as reactants 	<ul style="list-style-type: none"> ZnCuGa LDH selectively produces CH₃OH: 179 nmol g⁻¹ h⁻¹ (68 mol.%, selectivity) and CO: 79 nmol g⁻¹ h⁻¹ ZnCuAl LDH was selective to produce CO: 82 nmol g⁻¹ h⁻¹ with a selectivity of 94 mol.% 	<ul style="list-style-type: none"> LDH prepared were UV-Vis light active material with improved CO₂ adsorption The inclusion of Cu sites improves the CH₃OH selectivity The key to CH₃OH vs. CO selectivity was attributed to the binding nature of CO₂ at Cu species in form of carbonates 	[45]
ZnCuGa[Cu(OH) ₄ LDH	<ul style="list-style-type: none"> Development of ZnCuGa[Cu(OH)₄ LDH by replacing the anions in ZnCuGa[CO₃ and investigation of metal cations composition ratio of product selectivity and CO₂ photoreduction efficiency 	<ul style="list-style-type: none"> UV-visible light obtained from 500 W Xenon arc lamp CO₂ with H₂ gas as a reductant 	<ul style="list-style-type: none"> Photoreduction of CO₂ to CH₃OH for Zn₃Ga[Cu(OH)₄ LDH was obtained 0.49 μmol g⁻¹ h⁻¹ with 88 mol.% selectivity which is 5.9 times higher as compared to ZnCuGa[CO₃ 	<ul style="list-style-type: none"> The stearic availability for the [Cu(OH)₄]²⁻ is attributed to play the role in enhanced CH₃OH formation rate The narrower bandgap value also contributes to the photocatalytic performance The hydroxy groups bounded to Cu sites plays an important role in the CH₃OH production 	[46]

Table 1. Cont.

LDH Photocatalysts	Research Objective	Light Source and Reactants Employed	Photocatalytic Activity, CO ₂ Conversion to Value Added Chemicals	Parameters Contributing towards Improved Performance	Ref
Various M-Al (M = Mg, Zn and Ni) LDH and M-Ni LDH (where M = Mg, Zn) prepared from aqueous solution of metal nitrates and chlorides	<ul style="list-style-type: none"> Investigation of the effect of different metal salts precursor Analysis of metals cations ratio variation of photocatalytic activity Study of CO₂ photoreduction in aqueous solution of salts (NaCl, KCl, Na₂CO₃, NaHCO₃) 	<ul style="list-style-type: none"> UV-visible light Obtained from 400 W Hg high pressure lamp CO₂ with H₂O and aqueous solution of salts (NaCl, KCl, Na₂CO₃, NaHCO₃) were used in a closed system 	<ul style="list-style-type: none"> Maximum yield was obtained for Ni-Al LDH (Ni/Al = 4), synthesized by chloride metal salt employing 500 mg of photocatalyst in 350 mL of 0.1 M NaCl aqueous solution CO: 36.6 µmol CH₄: 0.7 µmol H₂: 12.2 µmol 	<ul style="list-style-type: none"> The Ni-Al LDH prepared by chloride metal salt precursor compensate the photogenerated charges well than LDH prepared from NO₃ salts CO₂ photoreduction in NaCl solution exhibits maximum performance which was attributed to the presence of interlayer Cl[−] ion in aqueous solution acting as a hole scavenger under UV light irradiation 	[47]
Ni-Al LDH (Chloride ion, Cl [−] effect)	<ul style="list-style-type: none"> Investigation regarding the Cl[−] ion effect as a holes scavenger on CO₂ photoreduction 	<ul style="list-style-type: none"> UV-visible light Obtained from 400 W high pressure Hg lamp CO₂ bubbled in aqueous solution of the NaCl containing suspended photocatalyst 	<ul style="list-style-type: none"> Ni-Al LDH within 0.1 M NaCl solution, 0.5 g of suspended photocatalysts and 8 h of light irradiation produces: CO: 56.4 µmol H₂: 9.3 µmol with selectivity towards CO of 86 mol. % After 29 h of irradiation CO: 110.9 µmol with selectivity towards CO of 88.4 mol. % 	<ul style="list-style-type: none"> The chloride ions (Cl[−]) in the aqueous solution of NaCl improved the CO₂ reduction via clear suppression of H₂ production and acts as an efficient hole scavenger 	[48]

Table 1. Cont.

LDH Photocatalysts	Research Objective	Light Source and Reactants Employed	Photocatalytic Activity, CO ₂ Conversion to Value Added Chemicals	Parameters Contributing towards Improved Performance	Ref
Fluorinated Ni-Al LDH and Fluorinated Mg-Al LDH	<ul style="list-style-type: none"> Investigation of fluorination of LDH surfaces and its effect on CO₂ photoreduction in aqueous solution. 	<ul style="list-style-type: none"> UV-visible light obtained from 400 W Hg high pressure lamp CO₂ bubbled in water with suspended photocatalysts 	<ul style="list-style-type: none"> Fluorinated Ni-Al LDH, with 7.5 ratio of Na₂AlF₆ in total Al species (Na₂AlF₆ + AlCl₃) with 0.5 g suspended photocatalysts in 350 mL of 0.1 M NaCl solution The maximum CO₂ conversion rate producing CO: 93.3 µmol after 20 h irradiation and selectivity of 80% 	<ul style="list-style-type: none"> Fluorination incorporates the (AlF₆)⁻³ units in LDH sheets, an important parameter leading to better CO₂ adsorption and Cl⁻ ion in aqueous solution suppressing H₂ formation and acting as a hole scavenger 	[49]
Mg-Al LDH	<ul style="list-style-type: none"> Investigating the effect of various Mg⁺² precursor (acetates and nitrates) and microwave irradiation time for conversion of CO₂ by Mg-Al LDH 	<ul style="list-style-type: none"> Solar simulator using 150 W Xe lamp Reaction is carried out in both liquid and gas phase with CO₂ and H₂O as reactants 	<ul style="list-style-type: none"> Mg-Al LDH synthesized using acetate precursor and 40 min of microwave irradiation yielded higher solar products in both liquid and gas phase Liquid Phase maximum CH₃OH: 9 µmol g⁻¹ h⁻¹ Gas Phase CO: 1.3 µmol g⁻¹ h⁻¹ CH₄: 0.4 µmol g⁻¹ h⁻¹ 	<ul style="list-style-type: none"> An optimal cut off various parameters enhanced the photocatalytic performance which includes the following: LDH Crystallinity Flat band potential CO₂ adsorption Charge transfer resistance 	[50]

Table 1. Cont.

LDH Photocatalysts	Research Objective	Light Source and Reactants Employed	Photocatalytic Activity, CO ₂ Conversion to Value Added Chemicals	Parameters Contributing towards Improved Performance	Ref
Co-Al LDH	<ul style="list-style-type: none"> The nanosheets of Co-Al LDH were synthesized and applied for atmospheric CO₂ conversion to useful products CO and CH₄ 	<ul style="list-style-type: none"> Simulated solar light obtained using 500 W Xe lamp CO₂ and H₂O vapors were employed as reactants under gaseous closed system 	<ul style="list-style-type: none"> Co-Al LDH nanosheets yielded CH₄: 4.3 $\mu\text{mol g}^{-1} \text{h}^{-1}$ after 5 h of irradiation and the yield reaches to 90% selectivity in 55 h of reaction 	<ul style="list-style-type: none"> Better light adsorption as band gap is 2.1 eV Surface alkaline OH groups for better CO₂ adsorption Divalent Co for efficient water splitting producing H₂ for hydrogenation reactions 	[51]
Nano crystals of Ni-Al LDH	<ul style="list-style-type: none"> Development of nanocrystals of Ni-Al LDH for enhanced CO₂ photoreduction 	<ul style="list-style-type: none"> Light is obtained from Hg high pressure Lamp of 400W CO₂ gas was bubbled through aqueous solution of 0.1 M NaCl with suspended photocatalyst (1.0 g) 	<ul style="list-style-type: none"> Ni-Al LDH synthesized from nanocrystals (around 20 nm) produces CO: 50 $\mu\text{mol h}^{-1}$, which is 7 times greater than standard crystalline Ni-Al LDH 	<ul style="list-style-type: none"> The high surface affinity of the nano Ni-Al LDH to CO₂ is attributed to the enhanced performance Such specific surface property is related to the quenching of the metastable surface by rapid hydroxide formation from the respective molten salts 	[52]
Ultrathin magnetic Mg-Al LDH represented as Fe ₃ O ₄ /Mg-Al LDH	<ul style="list-style-type: none"> Synthesis of 2-D ultrathin magnetic Mg-Al LDH by coupling with Fe₃O₄ for enhanced CO₂ photoreduction and recyclability of the photocatalyst 	<ul style="list-style-type: none"> Ultraviolet light is obtained from 8 W lamp CO₂ gas was passed through solution of 0.1 M NaOH (70 mL) and acetonitrile (5 mL) with photocatalyst (0.05 g) suspended in it 	<ul style="list-style-type: none"> Fe₃O₄/Mg-Al LDH with 10% of Fe₃O₄ content exhibited the maximum yield with production rate of, CO: 442.3 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CH₄: 223.9 $\mu\text{mol g}^{-1} \text{h}^{-1}$ 	<ul style="list-style-type: none"> Fe₃O₄ induces synergetic effect of photogenerated charges separation The 2D ultra-thin Mg-Al LDH also reduces the transmission resistance of charge carriers resulting in increased reactions sites 	[53]

Table 1. Cont.

LDH Photocatalysts	Research Objective	Light Source and Reactants Employed	Photocatalytic Activity, CO ₂ Conversion to Value Added Chemicals	Parameters Contributing towards Improved Performance	Ref
u-MAl LDH, where M = Mg ²⁺ , Co ²⁺ , Ni ²⁺ , and Zn ²⁺	<ul style="list-style-type: none"> Development of ultrathin LDH photocatalysts under 600 nm irradiation for high performance CO₂ reduction 	<ul style="list-style-type: none"> Light is obtained (400–800 nm) from Xenon Lamp of 300 W CO₂ was bubbled through the solution containing TEOA/H₂O/CH₃CN with dispersed photocatalysts and Ru based photosensitizer 	<ul style="list-style-type: none"> u-CoAl LDH yielded the maximum products containing: <ul style="list-style-type: none"> With 10 mg sample CO: 2.52 mol g^{−1} h^{−1} With 0.05 mg sample CO: 218.13 mmol g^{−1} h^{−1} With 0.05 mg sample under irradiation of 600 nm wavelength light CO: 43.73 mmol g^{−1} h^{−1} 	<ul style="list-style-type: none"> Abundant availability of vacancies in terms of V_o and V_M enhances the photocatalytic performance due to enhanced charge transport and separation 	[54]
Zn based LHD, represented by ZnM-LDH, where M = Ti, Fe, Co, Ga, and Al	<ul style="list-style-type: none"> To investigate the role of trivalent and tetravalent metal cations in the LDH towards CO₂ photoreduction and product selectivity 	<ul style="list-style-type: none"> UV light is obtained from Xenon lamp of 300 W with wavelength of 400–800 nm The water and photocatalyst are spread on the base of the reaction chamber and CO₂ gas is introduced to the reactor 	<ul style="list-style-type: none"> Zn-Ti LDH produces CH₄: 1.2 μmol g^{−1} h^{−1} H₂: 0.7 μmol g^{−1} h^{−1} with selectivity of 68% to CH₄ Zn-Al LDH yielded CO: 1.3 μmol g^{−1} h^{−1} with selectivity of 90% to CO Zn-Ga LDH produces CO: 1.6 μmol g^{−1} h^{−1} with selectivity of 78% to CO Zn-Fe LDH yielded H₂: 1.8 μmol g^{−1} h^{−1} with selectivity of 100% to H₂ Zn-Co LDH yielded H₂: 1.1 μmol g^{−1} h^{−1} with selectivity of 100% to H₂ 	<ul style="list-style-type: none"> Trivalent and tetravalent metal cations improved alters the selectivity of the products The metal ions with d-band centers relatively close to Fermi level strongly adsorb the CO₂ and produced CH₄ or CO dominantly Whereas the metal ions with d-band centers far from Fermi level poorly adsorb the CO₂ and yielded H₂ as a major product 	[55]

Table 1. Cont.

LDH Photocatalysts	Research Objective	Light Source and Reactants Employed	Photocatalytic Activity, CO ₂ Conversion to Value Added Chemicals	Parameters Contributing towards Improved Performance	Ref
NiO Nano sheets synthesized from oxidation of NiAl-LDH	<ul style="list-style-type: none"> Synthesis approach for thin NiO sheets having Ni and O vacancies via oxidation of NiAl-LDH 	<ul style="list-style-type: none"> Light irradiation was obtained from 300 W Xe lamp (300–800 nm) The reaction occurred in liquid phase with CO₂ bubbled through water/acetonitrile mixture, Ru based photosensitizer and TEOA as a sacrificial agent 	<ul style="list-style-type: none"> NiO nanosheets produced at a temperature of 275 °C, represented by NiAl-275 showed the maximum product yield, i.e., CH₄: 95 µmol g⁻¹ h⁻¹ 	<ul style="list-style-type: none"> At the optimum temperature, i.e., 275 °C, a special increase in the concentration's special structure with optimized defects of Ni and oxygen is achieved, which tunes the selectivity and performance of the photocatalyst 	[56]

Figure 10. (a) Schematic view of the synthesis approach developed for obtaining NiO photocatalyst. (b) Photocatalytic CO₂ conversion to useful chemicals. (c) Selectivity for various NiAl-LDH photocatalysts, oxidized at various temperatures as represented by temperature value after name. (Figures taken with permission from reference [56]. Copyright 2020, Elsevier).

4. Metals Loaded/Embedded Layered Double Hydroxide (LDH) Photocatalysts

Another effective strategy for the development of efficient LDH photocatalysts is to couple, embed, or dope the metals/non-metals to LDH structures, which will lead to improved photocatalytic performance in terms of CO₂ photo-reduction. Until today, a limited amount of investigations has been done with respect to mentioned domain; however, there exists an enormous potential to develop metals embedded or doped LDH, which might result in an enhanced and efficient photocatalytic CO₂ conversion to useful chemicals/fuels.

Zhao et al. reported a Ti embedded MgAl-LDH (MgAlTi-LDH) synthesized by three different methodologies and their performance evaluated by photocatalytic CO₂ conversion with water to useful products [57]. The three different synthesis methodologies include (i) co-precipitation (CP), (ii) co-precipitation and hydrothermal (HT), and (iii) co-precipitation followed by calcination and reconstruction (R). It was observed that the two key factors influencing the photocatalytic activity were crystallinity and surface area of the prepared samples. Moreover, the effect of the temperature treatment was also investigated in accordance with the photocatalytic performance. Figure 11a shows the surface morphologies for the MgAlTi-LDH samples synthesized by coprecipitation method followed by HT and R treatment at various temperatures, respectively. It was observed that the CP samples hydrothermally treated at different temperatures go under transformation of their small nanoflakes (50 nm) to large nanoflakes with increased size (500–1000 nm). Such transformation indicates the increase of crystallite size, which was also confirmed by XRD data. On the other hand, calcinated and reconstructed samples (R-MgAlTi LDH) do not exhibit any significant change in the crystallite size with the increase of the temperature. When employed for photocatalytic CO₂ tests, all samples exhibited better CO yield as compared to standard TiO₂-P25. Figure 11b,c show the photocatalytic CO₂ conversion to CO normalized by catalyst mass and surface area, respectively. It was noticed that HT150 and HT200 samples (hydrothermally treated sample at 150 and 200 °C) exhibit best performance

in accordance with both parameters, which can be attributed to the optimum condition of TiO₂ crystallinity, crystallite size, band gap, and surface area of the LDH photocatalyst.

Figure 11. (a) SEM images for the MgAlTi-LDH samples synthesized by coprecipitation approach followed by hydrothermal treatment (HT100, HT150, and HT200) and coprecipitation followed by calcination and reconstruction (R400, R500, and R600); the number represents the temperature value. (b) Photocatalytic CO production rate normalized as amount of TiO₂ present in the LDH photocatalysts and (c) normalized per surface area of the LDH photocatalysts synthesized. (Figures taken from [57]. Copyright 2016, Elsevier).

A research work reported by Iguchi et al. presented extension of their previously reported work by modifying the MgAl LDH with Ga₂O₃ and loading Ag nanoparticles on it [58]. It was observed that by loading 0.25 wt.% of Ag co-catalyst of Ga₂O₃-MgAl LDH, the photocatalytic CO₂ conversion to CO was improved with enhanced selectivity towards CO. The molar concentration of already prepared MgAl LDH was varied in order to optimize the sample with the best performance. It was observed the sample with 95 molar concentration and 0.25 wt.% of loaded Ag co-catalyst, exhibited the best performance, yielding 211.7 μmol/h with 0.19 g of photocatalyst. Such an increased yield was associated to the enhanced CO₂ adsorption by MgAl LDH, improving surface areas and selectivity induced by Ag nanoparticles.

Another research investigated by Chong et al. presents the role of MgAl-LDO as an interlayer in between Pt and TiO₂ for CO₂ photo-reduction to useful chemicals [59]. It was observed that the insertion of MgAl-LDO layer boosts the photocatalytic CO₂ conversion to CO and CH₄ as compared to reference samples. The authors used rutile TiO₂ rods, as they are more active for water oxidation, thus providing more protons and electrons, which can be utilized for CO₂ photo-reduction. The MgAl-LDH was in situ deposited and then calcined at high temperature to give LDO upon which the Pt (fixed 1 wt.%) was deposited. The sample optimization was performed by varying the loading amount of MgAl-LDH on the TiO₂ surface. It was observed that there exist no significant changes in the sample crystallinity, surface morphology, and surface areas. Figure 12a–c shows TEM images for the Pt-MgAl-LDO-TiO₂

photocatalyst with clear depiction of the MgAl-LDO interlayer and Pt deposition. Figure 12d shows the photocatalytic CO and CH₄ evolution rate from CO₂ photo-reduction and it can be noticed that Pt-MgAl-LDO-TiO₂ exhibit the highest production rate as compared to all other samples. The key parameter for promoting and enhancing the photocatalytic CO₂ conversion is synergetic effect of Pt deposition and interlayer of MgAl-LDO. It was proposed that the thin layer of MgAl-LDO optimized by MgAl-LDO deposition promotes the CO₂ adsorption and efficient transfer of photogenerated electrons to Pt where the CO₂ photo-reduction can occur. Moreover, the Pt nanoparticles act as electron sinks, and once they receive the photoexcited electrons, it is difficult for them to go back and recombine. The proposed reaction mechanism is well displayed in Figure 12e.

Figure 12. (a–c) TEM images for the Pt-MgAl-LDO-TiO₂ indicating the presence of interlayer MgAl-LDO between Pt nanoparticles and rutile TiO₂ nanorods. (d) CO and CH₄ evolution rate for all samples synthesized when employed for photocatalytic CO₂ conversion. (e) Proposed mechanism involved in the photocatalytic CO₂ conversion to CO and CH₄ on the surface of Pt-MgAl-LDO-TiO₂. (Figures taken from [59]. Copyright 2018, Elsevier).

Another research conducted by Wang et al. developed series of palladium (Pd) loaded CoAl-LDH (Pd/CoAl-LDH) photocatalysts with varied content of Pd, in combination with a ruthenium-based complex acting as a photosensitizer [60]. When these photocatalysts employed for photocatalytic CO₂ conversion, the syngas CO/H₂ was the major product, where Pd promotes the production of H₂ and CoAl-LDH yielded CO under visible light irradiation even when extended above 600 nm. It was observed that the ratio of CO/H₂ can be tuned by varying the loading of Pd nanoparticles. Figure 13a,b show the production rate of CO/H₂ and selectivity with varying the ratio of Pd. It can be noticed that with increasing the Pd amount, the relative amount of H₂ is increased due to reduction of protons. As Pd is a well-known H₂ producing cocatalyst, H₂ is produced by Pd, which captures the photogenerated electrons from the LDH, whereas the photogenerated electrons within the LDH can directly react with the adsorbed CO₂ to convert it into CO. The proposed mechanism of the CO₂ photo-reduction over the prepared photocatalysts is shown in Figure 13c where triethanolamine (TEOA) assists to regenerate the Ru based photosensitizer.

The summarized overview of up to date developed metal embedded/loaded LDH photocatalysts employed for photocatalytic CO₂ conversion to useful chemicals are presented in Table 2 in respect to research objective, reaction conditions, products yielded, and important influential parameters contributing to enhanced performance.

Table 2. Summary of various metal loaded/embedded LDH photocatalysts with research goal, reaction conditions, value added chemicals production by photocatalytic CO₂ conversion, and key parameters for improving performance.

LDH Photo Catalysts + Composite	Research Objective	Light Source and Reactants Employed	Photo Catalytic Activity, CO ₂ Conversion to Value Added Chemicals	Parameters Contributing towards Improved Performance	Ref.
Ti-embedded MgAl LDH represented as MgAlTi-LDH	<ul style="list-style-type: none"> Development of a ternary LDH Exploration of three different synthesis approaches and investigation of LDH photocatalysts for CO₂ photoreduction 	<ul style="list-style-type: none"> UV-Vis light Obtained from 400 W Xe lamp providing light in the range of 200–1000 nm. CO₂ gas was bubbled through H₂O towards the reactor for PCC 	<ul style="list-style-type: none"> Only CO was detected as a main product for all samples with minor CH₄ The sample which was synthesized by co-precipitation approach and followed by hydrothermal treatment at 150 °C showed the best CO yield of CO: 50 µmol for 5 h of irradiation normalized per g of TiO₂ 	<ul style="list-style-type: none"> Band gap, specific surface area, TiO₂ crystallinity, and crystallite size; all these factors contributed to the improved photocatalytic activity 	[57]
Pt-MgAl-LDO-TiO ₂	<ul style="list-style-type: none"> Development of an efficient LDO photocatalysts via introduction of MgAl LDO at interface of TiO₂ and Pt nanoparticles 	<ul style="list-style-type: none"> Light is obtained from 300 W Xenon lamp CO₂ with H₂O vapor were used as reactants 	<ul style="list-style-type: none"> The CO₂ photoreduction to useful chemicals for all samples were as follows: Bare TiO₂ sample CO: 0.016 µmol g⁻¹ h⁻¹ CH₄: 0.004 µmol g⁻¹ h⁻¹ Pt-MgAl-LDO/TiO₂-n samples, where n = 1,2, 5 representing the volume of MgAl colloidal solution Pt-MgAl-LDO/TiO₂-1 CO: 0.028 µmol g⁻¹ h⁻¹ CH₄: 0.038 µmol g⁻¹ h⁻¹ Pt-MgAl-LDO/TiO₂-2 CO: 0.038 µmol g⁻¹ h⁻¹ CH₄: 0.046 µmol g⁻¹ h⁻¹ Pt-MgAl-LDO/TiO₂-5 CO: 0.026 µmol g⁻¹ h⁻¹ CH₄: 0.032 µmol g⁻¹ h⁻¹ Pt-MgAl-LDO/TiO₂-10 CO: 0.018 µmol g⁻¹ h⁻¹ CH₄: 0.024 µmol g⁻¹ h⁻¹ 	<ul style="list-style-type: none"> Enhanced adsorption of CO₂ on MgAl-LDH surface and thus easiness of its dissociation with H₂O molecules Efficient photogenerated charge separation by Pt leading to improved CO₂ photoreduction 	[59]

Table 2. Cont.

LDH Photo Catalysts + Composite	Research Objective	Light Source and Reactants Employed	Photo Catalytic Activity, CO ₂ Conversion to Value Added Chemicals	Parameters Contributing towards Improved Performance	Ref.
Pd/CoAl-LDH and Ru based photosensitizer	<ul style="list-style-type: none"> Development of an efficient heterostructure for photocatalytic CO₂ conversion to syngas under light irradiation 	<ul style="list-style-type: none"> CO₂ reduction carried out under visible light irradiation with wavelength more than 400 nm and in gaseous phase 	<ul style="list-style-type: none"> Pd/CoAl-LDH and Ru based photosensitizer increase the tunable syngas (CO/H₂) molar ratio from 1:0.74 to 1:3 under visible light irradiation 	<ul style="list-style-type: none"> The presence of Pd NPs lead to well adsorb the water molecules which lead to formation of H₂ during light irradiation thus providing a pathway to tune the CO to H₂ ratio 	[60]

Figure 13. (a) Photocatalytic evolution syngas via CO₂ photo-reduction for varied amount Pd loaded CoAl-LDH (Pd/CoAl-LDH) photocatalysts. (b) Selectivity of prepared LDH photocatalysts towards CO and H₂ production with increased Pd content. (c) Proposed mechanism involved in the photocatalytic CO₂ conversion to CO and H₂ on the surface of Pd/CoAl-LDH photocatalyst. (Figures taken from [60]. Copyright 2019, Elsevier).

5. Composite/Hybrid/Heterojunctioned Layered Double Hydroxide (LDH) Based Photocatalysts

The fabrication of hybrid/heterojunctioned photocatalyst materials has always been an attractive and fascinating domain for the material scientists/researchers. As a well-explored domain, a similar approach is also implicated for the synthesis of hybrid/heterojunctioned photocatalysts employing LDH as one of the components with another established semiconductor material. The LDH support can act as an adsorbent and/or photocatalyst support to capture/convert CO₂ into useful products. Hence, the benefits and gains of the hybrid/heterojunctioned materials can be a harvested for CO₂ reduction by designing a suitable LDH based hybrid photocatalysts. With plenty of research space, until now, very limited investigations have been done with the respective concept.

A research work reported by Zhao et al. displays hybrid photocatalysts composed of MgAl-LDO coupled with TiO₂ cuboids (MgAl-LDO/TiO₂) [61]. The photocatalyst was synthesized by the combined approach of hydrothermal and coprecipitation methodologies, and a series of MgAl-LDO/TiO₂ was prepared with varied molar ratio of Mg + Al to Ti, in order to optimize the photocatalyst with best performance. As the MgAl-LDO are reported to be in micrometer size platelets, it was required to synthesize micrometer size TiO₂ which were synthesized in micrometer sized cuboids. Figure 14a–f shows the morphology of various MgAl-LDO/TiO₂ photocatalysts with varied ratio of Mg + Al. It is

obvious that MgAl-LDO platelets were successfully anchored on the TiO_2 cuboids even after calcination and do not change the morphology. Hence, this report is also unique in terms of morphology of the photocatalyst obtained. When employed for CO_2 photo-reduction with water vapors under UV light irradiation, CO was found to be the main product with small amount of CH_4 . Figure 14g shows the CO production rate by photocatalytic CO_2 conversion. It was observed that at a condition of UV light irradiation (4 h) and 50°C , MgAl-LDO alone had no activity, and also, when coupled with the TiO_2 , it did not show any significant photocatalytic activity towards CO_2 conversion to CO. This might be due to weak CO_2 adsorption at lower temperatures by MgAl-LDO. However, at higher temperature, i.e., 150°C , the 10% Mg-Al LDO/ TiO_2 showed a 5 times higher CO production as compared to bare TiO_2 cuboids. Moreover, 10% MgAl-LDO/ TiO_2 also exhibited the best performance, hence optimizing the Mg + Al ratio to Ti. Such an enhanced CO production can be attributed to the improved adsorption capacity of MgAl-LDO at higher temperatures. Upon illumination, the photogenerated electron in TiO_2 can easily transfer to the nearby interface of MgAl-LDO and TiO_2 , where it can react with adsorbed CO_2 converting it into CO. Figure 14h shows control tests of 10% MgAl-LDO/ TiO_2 under He gas and water vapors as reactants. It was observed that, at a temperature of 50°C , 10% MgAl-LDO/ TiO_2 does not show any CO yield; however, at a temperature of 150°C , a considerable amount of CO was observed. It was proposed that such CO might be a result of carbonate species on the surface of photocatalyst, which was stable at lower temperature, but at higher temperature, it was converted into CO.

Figure 14. SEM images of MgAl-LDO/ TiO_2 composites: (a,b) 8% MgAl-LDO/ TiO_2 , (c,d) 10% MgAl-LDO/ TiO_2 , and (e,f) 12 wt.% MgAl-LDO/ TiO_2 . Photocatalytic CO_2 conversion into CO employing (g) all samples at varied temperature, and (h) 10 wt.% MgAl-LDO/ TiO_2 under $\text{CO}_2 + \text{H}_2\text{O}$ and He + H_2O gaseous composition. (Figures taken with permission from reference [61]. Copyrights 2015, The Royal Society of Chemistry).

Another work performed by Kumar et al. investigated the heterojunction of CoAl-LDH with P25, a well-known standard TiO_2 [62]. P25 nanoparticles were encapsulated within microporous CoAl-LDH by a simple one step hydrothermal approach. It was observed that light absorption of the composite CoAl-LDH -P25 was red shifted, thus capturing the solar spectrum which might lead to improved photocatalytic activity. Furthermore, the CO_2 adsorption capacity and matched band alignment also promote the efficient conversion of CO_2 into useful chemicals. Figure 15a,b shows the morphology of the P25@CoAl-LDH photocatalyst with clear depiction of 2D platelets of CoAl LDH with thickness of approximately 20 nm and irregular nanoparticles of P25 within size range of 20–50 nm. Figure 15c shows the UV–Vis DRS for all the samples investigated in the research work. P25 showed its characteristic absorption in the UV range with the absorption peak centered around 300 nm, whereas CoAl-LDH exhibited two absorption peaks appearing in the UV and visible range, respectively. The absorption peak appearing around 500 nm was attributed to the d–d transitions of octahedral Co^{2+} . Figure 15d shows the steady state photoluminescence (PL) spectroscopy for the samples. The PL peaks for P25@CoAl-LDH were intermediate between pure P25 and CoAl-LDH, thus endorsing the reduced charge recombination within the composite P25@CoAl-LDH photocatalyst. When employed for photocatalytic CO_2 conversion, only three products were formed, i.e., CO, H_2 , and O_2 , shown in Figure 16a–d. Pure P25 showed the poorest activity with negligible production; however, CoAl-LDH exhibited certain amount of CO and O_2 production. P25@CoAl-LDH showed a production in between P25 and CoAl-LDH, whereas 20 wt.% P25@CoAl-LDH showed a superior production of CO with negligible amount of CH_4 . Such an increased CO production and higher selectivity can be attributed to the well heterojunction formation within P25@CoAl-LDH and was associated to extended light absorption, enhanced CO_2 adsorption, and effective photogenerated charges separation. Furthermore, the P25@CoAl-LDH sample also exhibited a stable performance up to 3 cycles of CO_2 photo-reduction. Figure 15e shows the band gap alignment and heterojunction formation for the P25@CoAl-LDH photocatalyst. As well established, band gap of P25 is suitable for proton reduction but not suitable for CO_2 photo-reduction. On the contrary, the bandgap of CoAl-LDH with its conduction band edge at -0.75 eV can easily produce CO. Thus, the combination of both P25 and CoAl-LDH leads to formation of p-n junction which is well aligned for the efficient production of CO and photogenerated charge separation, ultimately resulting in enhanced photocatalytic activity for CO_2 conversion into useful product.

A research work executed by Tang et al. demonstrated the synthesis of unique homo-heterojunction of BiOCl nanoplates coupled with ZnCr-LDH by a simple electrostatic interaction method [63]. As well-known BiOCl generally consists of two directions, that is, {001} and {110} surfaces. Both surfaces form a homojunction within the BiOCl, whereas the ZnCr-LDH can assemble on {001} surface via electrostatic interaction. A built-in field will allow the electrons generated under irradiation to flow from one facet to another facet of BiOCl, from where they can easily flow down to the coupled ZnCr-LDH and react with adsorbed CO_2 . Various samples were synthesized with different content of the ZnCr-LDH represented by “Sc” wt.%. Figure 17a shows the photocatalytic CO_2 conversion for various BiOCl-ZnCr-LDH samples with different contents of ZnCr yielding CH_4 as a main product. The maximum yield was obtained when ZnCr-LDH amount was 10 wt.%. The proposed mechanism for charge transfer within BiOCl homojunction and heterojunction with ZnCr-LDH is shown in Figure 17b. The key factor indulged in the performance improvement was the efficient charge transfer.

Another research work executed by Yang and coauthors proposed an urchinlike Z-scheme photocatalyst by hierarchical structure of CoZnAl-LDH/RGO/g- C_3N_4 (LDH/RGO/CN) [64]. The LDH was synthesized by simple hydrothermal method, while for the synthesis of LDH/RGO/CN, the already prepared RGO and CN were added into the ionic precursors of LDH and then subjected for hydrothermal process. For the sake of optimization and achieving of best sample, the weight ratio of CN was varied among the LDH/RGO/CN hybrid photocatalyst. The schematic view of the synthesis procedure designed to achieve LDH/RGO/CN is shown in Figure 18a. The morphologies of CN and LDH/RGO/CN

are shown in Figure 18b,c, respectively. The CN exhibited a bulky morphology with somewhat lamellar structures, whereas LDH/RGO/CN exhibited a well observable urchin like nanostructure. When employed for photocatalytic CO₂ conversion, CO was observed as the key product, with CH₄ up to 5 h of irradiation; it is shown in Figure 18d,e. It could be noticed that insertion of RGO between CoZnAl-LDH and CN significantly enhanced the CO yield, specifically for sample LDH/RGO/CN-2 (with 0.1 g of CN in the composite) whose CO yield was 3.4 and 8.5 times higher than LDH/CN and bare CN, respectively. As well established, CO₂ adsorption and photocatalytic activity are two prime contributors for efficient photocatalytic CO₂ conversion. The ternary composite of CoZnAl-LDH shows improved CO₂ adsorption whereas CN is well known for its visible light activity. In addition, the insertion of RGO promotes the efficient charge separation from CoZnAl-LDH to valence band of CN, whereas the holes of CoZnAl-LDH are generated by water oxidation. The proposed schematic based on several analysis techniques is displayed in Figure 18f.

Figure 15. (a) High resolution SEM image and (b) TEM image of 20 wt.% P25@CoAl-LDH. (c) UV-Vis DRS and (d) PL spectra for all the samples employed in the research. (Figures taken with permission from reference [62]. Copyright 1969, Elsevier).

Figure 16. (a) Schematic diagram of the heterojunction formation between P25 and CoAl-LDH. Photocatalytic CO_2 conversion to (b) CO, (c) H_2 , (d) O_2 , and (e) stability evaluation for 20 wt.% P25@CoAl-LDH. (Figures taken with permission from reference [62]. Copyright 1969, Elsevier).

Figure 17. (a) Photocatalytic CO_2 conversion to CH_4 for various hybrid BiOCl-ZnCr-LDH photocatalysts, S represents the BiOCl-ZnCr-LDH sample with subscript indicating the composition of the ZnCr-LDH. (b) Schematic diagram of the heterojunction formation between BiOCl and ZnCr LDH. (Figures taken with permission from reference [63]. Copyrights 2018, The Royal Society of Chemistry).

Another excellent work done by Ziarati et al. reported an efficient architecture of 3D yolk@shell $\text{TiO}_{2-x}/\text{CoAl LDH}$ ($\text{Y@S TiO}_{2-x}/\text{LDH}$) for photocatalytic CO_2 conversion to solar fuels [65]. Such an architecture was synthesized by sequential designing of solvothermal, hydrogen treatment, and hydrothermal steps. When such a 3D architecture was employed for CO_2 photo-reduction, it yielded CH_3OH as a main product for the first 2 h of irradiation; however, the CH_3OH production decreased with the passage of time, and CH_4 yield increased. Figure 19a shows the CH_3OH production for the 3D architecture photocatalyst along with other reference samples. Figure 19b exhibits the time dependent photocatalytic CO_2 conversion to solar fuels. Such a conversion of product from CH_3OH to CH_4 is proposed, since, with the passage of time, CH_3OH gets adsorbed on the surface,

and photocatalytic is converted into CH_3 radical, which reacts with electron and protons to form CH_4 as the key product. The enhanced performance of the 3D photocatalyst was attributed to the combination of better CO_2 sorption capacity, improved light absorption, and enhanced charge separation at interface of TiO_{2-x} and LDH.

Figure 18. (a) Synthesis scheme of hybrid urchin like LDH/RGO/CN photocatalyst. SEM Images of (b) graphitic carbon nitride (CN), and (c) urchin-like CoZnAl-LDH . (d) Photocatalytic CO_2 conversion to CO for all samples. (e) Production rate of CO and minor CH_4 per hour from all samples. (f) Proposed mechanism for the heterojunctioned formation and photocatalytic CO_2 conversion to CO, mainly. (Figures taken with permission from reference [64]. Copyright 2019, Elsevier).

Figure 19. (a) Photocatalytic CO₂ conversion into CH₃OH (various samples). (b) Production rate of CH₃OH and CH₄ as a function of time over the hybrid LDH based photocatalyst. (Figures taken with permission from reference [65]. Copyright 2019 American Chemical Society).

Another approach represented an LDH based composite photocatalyst with doped strategy. Jo et al. developed a N doped C dots/ CoAl LDH/gC₃N₄ (NCD/LDH/CN, represented as NLC) hybrid photocatalyst with efficient and selective photocatalytic CO₂ conversion to CH₄ [66]. The N doped carbon dots (NCD) are well researched materials as an alternate to noble metals cocatalysts. In their work, co-authors designed a strategy to employ NCD in replacement of noble metals and found a significant increase and selective production of CH₄. Various NLC photocatalysts were synthesized by varying the contents of LDH to CN as 5, 10, 15, and 20 wt.%, whereas the amount of NCD was kept fixed for all samples, which was 2 wt.%. Figure 20a shows the SEM image of the NLC sample exhibiting a flower like morphology with clear depiction of LDH and CN. Figure 20b shows a high resolution TEM image of NLC with clear presence of all three components, i.e., LDH, CN, and NCD in the hybrid sample. When utilized for photocatalytic CO₂ conversion, the key product obtained was CH₄ with small amounts of CO and H₂, as shown in Figure 20c. It was observed when NLC is formed by 2 wt.% NCD and with LDH to CN ratio of 10, the sample NLC-10 exhibited the maximum production rate as compared to all other samples. The most remarkable selectivity was 99% towards CH₄ for NLC-10 sample. The reusability of the NLC-10 was also evaluated (shown in Figure 20d), which displayed a durable performance in each cycle, thus representing the stable performance during the prolonged reaction possibly to a good structural stability of the photocatalyst. The prime factors contributing to significantly improved photocatalytic performance of NLC consist of broadened light absorption, optimized surface area, and improved charge separation due to 2D junction in between LDH and CN. Moreover, the product selectivity was attributed to the well aligned band gap with corresponding product redox potential. The proposed mechanism for the photocatalytic CO₂ conversion employing NLC-10 sample is shown in Figure 20e. Under the visible light irradiation, both LDH and CN photogenerate the charges and electron flowing down to conduction band of LDH whereas holes from LDH towards the valence band of CN where they are regenerated by water oxidation. Due to formation of well-defined 2D–2D heterojunction between LDH and CN, the photogenerated charges are efficiently transferred and react with CO₂ adsorbed on the LDH surface. In addition, NCD also acts as electron sinks for efficient removal of electrons from conduction band of LDH to get reacted with adsorbed CO₂ and converted to CH₄.

Recently Wu and co-authors developed an efficient NiFe-LDH wrapped Cu₂O nanocube (NFC) heterostructure for enhanced photocatalytic CO₂ conversion [67]. The NFC photocatalysts were synthesized by a simple co-precipitation approach with varied time of aging temperature. Figure 21a–c shows the SEM images of NiFe-LDH, Cu₂O nanocubes and the NFC heterostructure photocatalyst, respectively. The NiFe-LDH consisted of interconnected layers resulting in a flower like morphology, whereas Cu₂O were in fine nanocubes. The NFC heterostructure shows a smooth structure of nanocubes covered with layers of LDH. The photocatalytic CO₂ conversion for NFC photocatalyst yielded mainly CH₄ as a key product. Figure 21d shows the CH₄ production rate for various samples with varied

aging time, i.e., 1, 2, and 4 h represented by NFC-1, NFC-2, and NFC-4, respectively. The NFC-4 displayed the highest efficiency amongst all the samples. The authors proposed a Z-scheme mechanism for conversion of CO_2 to CH_4 , shown in Figure 21e. It can be assumed that upon light irradiation, the electrons generated in Cu_2O react to the adsorbed CO_2 on NFC surface and are converted to CH_4 , while the holes in valence band are filled by the photogenerated electrons from LDH. Thus, the key factors involved for the enhanced efficiency include visible light absorption, efficient charge separation, and improved CO_2 adsorption.

Figure 20. (a,b) TEM images for the hybrid NLC-10 photocatalyst. (c) Photocatalytic CO_2 conversion from various samples to CO , H_2 , and CH_4 , with (d) stable performance evaluation. (e) Schematic for the proposed mechanism of CO_2 conversion to useful chemicals over the hybrid NLC photocatalyst surface. (Figures taken with permission from reference [66]. Copyright 2019, Elsevier).

Figure 21. SEM images of (a) NiFe-LDH, (b) Cu₂O Cuboids, and (c) hybrid NiFe-LDH-Cu₂O (NFC-4 Sample). (d) Photocatalytic CO₂ conversion from reference and various NFC samples to CH₄. (e) Proposed Z-scheme mechanism involved in PCC with band gap alignment. (Figures taken with permission from reference [67]. Copyright 2020, Elsevier).

Similarly, Jiang et al. reported Cu₂O loaded ZnCr LDH for CO₂ photo-reduction to useful fuels [68]. The Cu₂O@ZnCr LDH was synthesized by a ternary CuZnCr LDH via in situ reduction process. A variety of samples were prepared by in situ reduction of Cu_{2-x}Zn_{2-2x}Cr LDH (where $x = 0.05, 0.1, 0.2$, and 0.4) resulting in the formation of x Cu₂O@Zn_{2-2x}Cr LDH. The photocatalytic CO₂ conversion employing x Cu₂O@Zn_{2-2x}Cr LDH sample is shown in Figure 22a,b. The CO₂ conversion to mainly CO was observed from the samples with 0.1Cu₂O@Zn_{1.8}Cr LDH sample exhibiting the highest yield as compared to its corresponding reference samples (Figure 22a). The key behind the significantly enhanced activity after Cu loading was its superb electron extraction property from the photocatalyst. Figure 22c exhibits the CO₂ conversion of various x Cu₂O@Zn_{2-2x}Cr LDH samples, indicating the 0.1Cu₂O@Zn_{1.8}Cr LDH sample is the most efficient photocatalyst with optimized loading of Cu content. Moreover, the effect of various additives was also investigated for 0.1Cu₂O@Zn_{1.8}Cr LDH sample and is shown in Figure 22d. It was observed that Na₂SO₃ and Na₂CO₃ additives suppressed the formation of CO and enhanced the formation of H₂, due to their better hole scavenging properties and occupying the CO₂ adsorption sites. Figure 22e shows the proposed mechanism of CO₂ photo-reduction for 0.1Cu₂O@Zn_{1.8}Cr LDH sample. Upon light irradiation, the photogenerated electrons are extracted by Cu₂O nanoparticles where they react with adsorbed CO₂ species to yield CO. Hence the key role of Cu₂O nanoparticles on the surface of 0.1Cu₂O@Zn_{1.8}Cr LDH sample is an efficient electron separator providing CO₂ active sites.

Figure 22. Photocatalytic CO_2 conversion to CO and H_2 , (a) employing $0.1\text{Cu}_2\text{O}@Zn\text{Cr LDH}$ samples under CO_2 and Ar gaseous reactants; (b) amount of CO and H_2 yielded after 24 h of reaction for employing $0.1\text{Cu}_2\text{O}@Zn\text{Cr LDH}$ samples, (c) under CO_2 gaseous reactant for various $x\text{Cu}_2\text{O}@Zn\text{Cr LDH}$ samples; and (d) amount of CO and H_2 produced after 24 h for various $x\text{Cu}_2\text{O}@Zn\text{Cr LDH}$ samples. (e) Proposed mechanism involved in PCC with band gap alignment. (Figures taken with permission from reference [68]. Copyright 2017, Elsevier).

In another manner, LDH materials can be utilized as based material to synthesize efficient composite/heterojunctioned/hybrid photocatalysts. There are very limited reports regarding the utilization of LDH materials as photocatalyst precursors. To our best knowledge, in our investigation, we found a couple of research works taking advantage of mentioned approach and providing a novel pathway towards efficient photocatalysts development. Ye et al. reported CeO_{2-x} platelets from monometallic cerium LDH (MCE-LDH) and evaluated their performance for photocatalytic CO_2 conversion [69]. The synthesis approach consists of two steps including synthesis of MCE-LDH in the first step followed by second step of heat treatment at various temperatures up to 800°C . Figure 23a shows the SEM image of a synthesized un-calcined MCE-LDH displaying the quasi-hexagonal platelets. Figure 23b shows the SEM image of the MCE-LDH calcined at a temperature of 800°C , thus indicating that thermal treatment does not change significantly the structure except for the increased density of the nanopores. Figure 23c exhibits the UV-Vis DRS for various samples. It was observed that MCE-LDH exhibits broad hump at 320 nm , whereas when MCE-LDH were calcined, the absorption spectra showed two absorption peaks at 280 nm and 320 nm , corresponding to the Ce^{3+} and Ce^{4+} , respectively. The inset to UV-Vis DRS shows the absorption ratio for Ce^{3+} to Ce^{4+} with temperature. The MCE-LDH sample calcined at 800°C (MCE-LDH-800) shows the maximum ratio, whereas upon increasing the temperature up to 1000°C , the absorption ratio decreased due to structure distortion. Figure 23d displays the photocatalytic CO_2 conversion test with the synthesized and reference samples. It was observed that only CO was yielded, and sample calcined at 800°C yielded the maximum CO production rate, 2.5 times higher than reference CeO_2 . Moreover, the optimized sample MCE-LDH-800 shows a stable photocatalytic performance for 4 cycles (8 h of each cycle) of testing. The photocatalytic performance was believed to be enhanced by two key factors of $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox couple present at the surface of MCE-LDH and enhanced surface areas. The $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox couple supports in the efficient charge separation, whereas improved surface areas lead to increased active sites for CO_2 adsorption and conversion. The proposed mechanism by authors is shown in Figure 23e; under light irradiation, Ce^{4+} ions and oxygen vacancies will trap the photogenerated electrons. Such oxygen vacancy will promote the CO_2 adsorption which will react with Ce^{3+} ions and get converted to CO_2^- , which will further react with electron and proton to give CO. On the other hand, Ce^{3+} ions after reducing adsorbed CO_2 will be converted to Ce^{4+} ions, and thus, the reaction cycle continues.

The summary of the reviewed composite photocatalysts with LDH with respective research aims, reaction condition, solar fuels production, and various contributing parameters to catalytic performance is tabulated in Table 3.

Table 3. Summary of various LDH based composite photocatalysts with research goal, reaction conditions, value added chemicals production by photocatalytic CO₂ conversion, and key parameters for improved performance.

LDH Photo-Catalyst	Research Objective	Light Source and Reactants Employed	Photo-Catalytic Activity, CO ₂ Conversion to Value Added Chemicals	Parameters Contributing towards Improved Performance	Ref
MgAl-LDO/ TiO ₂	<ul style="list-style-type: none"> Investigation of MgAl-LDO/ TiO₂ composite photocatalysts for PCC by varying the ration of Mg + Al to Ti 	<ul style="list-style-type: none"> 50 W Xe lamp with a UV cut-off filter was used as a light irradiation CO₂ bubbled through water was used as a reactant 	<ul style="list-style-type: none"> Sample with 10 wt.% of MgAl-LDO TiO₂ yields the best performance with production rate of CO: 4.3 $\mu\text{mol g}^{-1} \text{h}^{-1}$ (under UV light) CO: 1.0 $\mu\text{mol g}^{-1} \text{h}^{-1}$ (under Visible light) 	<ul style="list-style-type: none"> Ratio of Mg + Al to Ti in the composite LDH enhances the CO₂ adsorption Under light irradiation, the photogenerated charges form TiO₂ can travel to adsorbed CO₂ and photoreduce to respective product 	[61]
P25@CoAl- LDH Nano Composite	<ul style="list-style-type: none"> A facile and cost-effective synthesis strategy for P25 encapsulated CoAl-LDH with improved CO₂ photoreduction 	<ul style="list-style-type: none"> UV-Vis and visible light is obtained from 300 W Xe lamp CO₂ gas was bubbled through water containing suspended photocatalyst 	<ul style="list-style-type: none"> 20 wt.% P25@CoAl-LDH yielded the best production rate of CO: 2.21 $\mu\text{mol g}^{-1} \text{h}^{-1}$ (UV-Vis light irradiation) CO: 0.714 $\mu\text{mol g}^{-1} \text{h}^{-1}$ (with visible light irradiation) 	<ul style="list-style-type: none"> The type II junctions formed between P25 and CoAl LDH lead to the efficient separation of photogenerated electro-hole pairs leading to enhanced CO yield The bandgap positions well aligned to produce selectively CO with a value of greater than 90% 	[62]
BiOCl-ZnCr- LDH	<ul style="list-style-type: none"> The development of homo-hetero junctioned BiOCl-ZnCr-LDH for efficient CO₂ photo-reduction 	<ul style="list-style-type: none"> Light is obtained from 500 W Xenon Lamp CO₂ bubbled through water was used as a reactant 	<ul style="list-style-type: none"> Stacking 10% wt.% of ZnCr-LDH with BiOCl resulted in the best photocatalytic performance with yielding CH₄: 0.86 $\mu\text{mol g}^{-1}$ (for 6 h irradiation) 	<ul style="list-style-type: none"> The composite formation of ZnCr-LDH with BiOCl, resulting in homo-hetero junctioned system which lead to improved holes separation and thus enhanced photocatalytic performance 	[63]

Table 3. Cont.

LDH Photo-Catalyst	Research Objective	Light Source and Reactants Employed	Photo-Catalytic Activity, CO ₂ Conversion to Value Added Chemicals	Parameters Contributing towards Improved Performance	Ref
In situ loaded RGO and g-C ₃ N ₄ on CoZnAl-LDH, represented by LDH/RGO/CN	<ul style="list-style-type: none"> Synthesis of a Z-scheme hybrid Photocatalysts Investigation of various components for improved CO₂ photoreduction 	<ul style="list-style-type: none"> Light is obtained from Xenon lamp of 300 W CO₂ gas and water vapors were employed as key reactants 	<ul style="list-style-type: none"> Bare CoZnAl-LDH produces CO: 5.99 $\mu\text{mol g}^{-1} \text{h}^{-1}$ Bare g-C₃N₄ produces CO: 10.69 $\mu\text{mol g}^{-1} \text{h}^{-1}$ LDH/CN produces CO: 15.06 $\mu\text{mol g}^{-1} \text{h}^{-1}$ LDH/RGO/CN-1 produces CO: 19.39 $\mu\text{mol g}^{-1} \text{h}^{-1}$ LDH/RGO/CN-2 produces CO: 50.53 $\mu\text{mol g}^{-1} \text{h}^{-1}$ LDH/RGO/CN-3 produces CO: 15 $\mu\text{mol g}^{-1} \text{h}^{-1}$ 	<ul style="list-style-type: none"> The optimum content of g-C₃N₄ provides the best performance due to increased charge lifetime and enhanced separation via Z-scheme mechanism The RGO acts as an electron mediator at the junction of CN and LDH 	[64]
Y@S TiO _{2-x} /LDH	<ul style="list-style-type: none"> Development of a novel 3-D nanoarchitecture for efficient CO₂ photoreduction Investigation of time dependent experiments for selective fuel/chemical production 	<ul style="list-style-type: none"> Light is obtained from Xenon lamp of 300 W CO₂ was bubbled through water and used as key reactants 	<ul style="list-style-type: none"> Y@S TiO_{2-x}/LDH yielded CH₃OH/CH₄ with respect to time of irradiation For 2 h of irradiation, the key product obtained was CH₃OH: 216 $\mu\text{mol g}^{-1} \text{h}^{-1}$ After 12 h of irradiation, the amounts of CH₃OH and CH₄ increased to 726 and 453 $\mu\text{mol g}^{-1}$, respectively 	<ul style="list-style-type: none"> Advanced architecture of Y@S TiO₂ containing oxygen vacancies linked with LDH plates enhances CO₂ absorption in defect sites and interlayerspaces Moreover, TiO_{2-x} provides a better light absorption with narrower band gap The time dependent selectivity was attributed to the conversion of radicals adsorbed to CH₄ and CH₃OH 	[65]

Table 3. Cont.

LDH Photo-Catalyst	Research Objective	Light Source and Reactants Employed	Photo-Catalytic Activity, CO ₂ Conversion to Value Added Chemicals	Parameters Contributing towards Improved Performance	Ref
NiFe-LDH wrapped Cu ₂ O nanocubes, (NFC)	<ul style="list-style-type: none"> Inexpensive and facile synthesis of Z-scheme 2-D NiFe-LDH and Cu₂O nanocubes for efficient CO₂ photoreduction 	<ul style="list-style-type: none"> Light is obtained from Xenon Bulb intensity of 300 W CO₂ gas was generated in situ by reaction of NaHCO₃ and H₂SO₄ 	<ul style="list-style-type: none"> NFC-4 with 4 hr of aging at 65 °C yielded the best solar fuel, i.e., CH₄ around 3.33 mmol g⁻¹ for 4 h irradiation, which is about 6.9 times of Cu₂O and 5.6 times of NiFe-LDH 	<ul style="list-style-type: none"> Z-scheme mechanism for charge separation and improved light absorption were the key reason for enhanced CH₄ yield 	[67]
xCu ₂ O@Zn _{2-2x} Cr LDH	<ul style="list-style-type: none"> Inexpensive facile strategy to synthesize the ternary LDH photocatalyst for efficient CO₂ photoreduction 	<ul style="list-style-type: none"> UV light is obtained from 200 W Xe lamp CO₂ was bubbled through DI water containing respective photocatalysts in suspended form 	<ul style="list-style-type: none"> Cu₂O@Zn_{2-2x}Cr LDH produces maximum yield of solar products (for 24 h), which contains, H₂: 41.2 µmol and CO: 0.8 µmol with additive of Na₂SO₄ 	<ul style="list-style-type: none"> The loaded Cu₂O nanoparticles acts as an efficient electron extractor from LDH photocatalyst The addition of Na₂SO₃ suppresses the generation of CO and promotes the water splitting leading to formation of H₂. 	[68]
Mono-metallic Cerium LDH (MCe-LDH)	<ul style="list-style-type: none"> Synthesis of MCe-LDH by a simple and facile approach Investigation of the heat treatment effect at various temperatures for CO₂ photoreduction 	<ul style="list-style-type: none"> UV-Vis light obtained from 300 W Xenon lamp CO₂ and water vapors were used as reactant in gaseous phase 	<ul style="list-style-type: none"> MCe-LDH heated upto 800 °C yielded the maximum CO yield of 13.4 µmol g⁻¹ in 8 h 	<ul style="list-style-type: none"> Heat treatment resulted in enhancement of concentration ratio of and increased surface area, both factors enhanced the photo reduction of CO₂ 	[69]

Figure 23. SEM images of (a) MCe-LDH and, (b) MCe-LDH calcined at 800 °C. (c) UV-Vis DRS spectra of the various reference and synthesized samples in the respective research work. (d) Photocatalytic CO₂ conversion from various MCe-LDH samples to CO. (e) Schematic of the mechanism involved in PCC with H₂O. (Figures taken with permission from reference [69]. Copyright 2017, Elsevier).

6. Conclusions

The review mainly focusses on the progress of LDH and LDH based photocatalysts for photocatalytic CO₂ conversion. The influential properties, reaction conditions, proposed mechanisms, and various influential aspects for photocatalytic CO₂ conversion were comprehensively explained. The interesting and mind captivating behavior of LDH photocatalysts for improved photocatalytic performance can be attributed to a combination of prime parameters which include (i) improved CO₂ adsorption, (ii) improved light absorption, (iii) improved separation of photogenerated charges, and (iv) better product selectivity due to band gap alignment. Furthermore, surface modification

of LDH, effect of various additives, noble metals loading/embedding, wrapping with graphene derivatives, and hybrid LDH based heterojunctioned photocatalysts were studied and explained principally. Conclusively, it can be inferred that LDH and/or LDH based photocatalysts open up a new way towards the alternate and efficient photocatalysts with a great potential for efficient photocatalytic CO₂ conversion into useful chemicals/fuels.

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