Layered double hydroxide-based photocatalytic materials toward renewable solar fuels production

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Abstract
Photocatalysis is an ideal and promising green technology to drive numerous chemical reactions for valued chemicals production under very mild conditions, thereby providing solutions to global energy and environment issues related to burning fossil fuels. Over the past decade, layered double hydroxides (LDHs), as the members in two-dimensional materials family, have attracted much attention due to their many advantages in photocatalysis, such as facile synthesis, low cost and powerful tunability of composition. In this review, we provide a synthetic overview of recent research advances of LDH-based photocatalysts, with the main discussion of the design strategies to improve their photocatalytic performance, including component control, defect engineering, hybridization, and topological transformation. Structure-performance correlations and tailor-made material synthesis strategies are elaborated to discuss how to realize high-performance LDH-based photocatalysts for three important reactions (i.e., water splitting, CO\textsubscript{2} conversion, and N\textsubscript{2} reduction) to generate desirable solar fuels. Further, the remaining challenges and future perspectives of LDH-based photocatalysts are summed up, aiming to inspire brand new solutions for pushing forward the development of LDH-based photocatalysis.

KEYWORDS
component control, defect engineering, layered double hydroxide, photocatalysis, solar fuels
Layered double hydroxides (LDHs) are important members of two-dimensional (2D) nanomaterials with a general formula \([\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2](\text{A}^{n-})_n\text{yH}_2\text{O}\), where typically \(\text{M}^{2+} = \text{Mg}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}\), and so forth, \(\text{M}^{3+} = \text{Al}^{3+}, \text{Cr}^{3+}, \text{Fe}^{3+}, \text{In}^{3+}, \text{Ga}^{3+}\), and so forth. \([\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]\) layers belong to brucite-like structure with positive charge, which are generally constituted by two or more kinds of bivalent and trivalent metal ions in the form of side-shared \(\text{M(OH)}_6\) octahedral units. \(\text{A}^{n-}\) represents the negative ion between the layers, typically \(\text{A}^{n-} = \text{CO}_3^{2-}, \text{Cl}^-, \text{F}^-, \text{NO}_3^-, \text{SO}_4^{2-}\) or other inorganic/organic anions. Furthermore, a variety of mixed metal oxides (MMO), hybrids of metal and metal oxide, alloys, nitrides, sulfides, and phosphides can be obtained facilely via a topological transformation of LDH precursors at specific temperature and atmosphere. The flexible components and various derivatives make LDHs adaptable to a variety of application fields such as energy storage, environmental protection, medical treatment, and catalysis. Among these crucial applications that have been explored to date, photocatalysis has emerged as a very promising candidate to replace traditional catalysis, owing to its environmentally friendly and low-energy-consumption features.

Since 1970, deteriorating issues of fossil fuel depletion and environmental damage have gained much more attention due to their horrifying potential causing a global energy crisis. The traditional chemical industry still faces severe energy-economy issues, which motivates the development of sustainable technologies to alleviate this consequence. Taking synthetic ammonia industry as an example, this process occupies nearly 2% and 1.6% of the world’s annual energy consumption and CO2 emission respectively, making it urgent to exploit sustainable energy source to drive this chemical reaction. Among a wide variety of sustainable and eco-friendly strategies, solar energy is deemed as one of the most seductive and promising candidates. The sun transmits energy to the earth at a rate of 120 000 TW, which is much larger than the estimated global energy consumption rate of 27.6 TW in 2050. Since the first example of solar energy utilization via photocatalysis was realized in 1972, photocatalysis has been widely concerned and investigated, and a lot of progresses have been achieved over the past few decades in environmental and energy fields, including photocatalytic degradation, organic synthesis, water splitting, \(\text{CO}_2\) and \(\text{N}_2\) reduction reaction. Although enormous advances in photocatalysis have been made, the solar-to-chemical conversion efficiency is still very low and far from meeting the actual demand. The development of new photocatalysts on the basis of different reaction characteristics for ameliorated performance is a pressing priority and technical challenge. For photocatalytic conversion of organic molecules (organic synthesis or pollutant degradation), outstanding photocatalytic performance mainly depends on the rapid generation of reactive oxygen species (H2O2, \(\text{O}_2^-.\), \(\text{OH}^-.\), and \(\text{-O}_2^-.\)). As for the photocatalytic reactions toward renewable solar fuels production, the weaker chemical reactivity of small molecules (H2O, CO2, and \(\text{N}_2\)) with high bond energy brings greater challenges for rational photocatalyst design, such as (1) high-energy photogenerated carriers; (2) multiple electrons transfer process; and (3) sufficient activation of reactants on the surface of catalyst. Recently, various photocatalysts have been screened out for systematic studies, such as \(\text{TiO}_2\), \(\text{BiOX}\), and \(\text{g-C}_3\text{N}_4\), among others. Benefiting from the adjustable size, bandgap, and surface property, LDH-based photocatalytic materials have exhibited exciting performance and application prospects toward renewable solar fuels production.

In this review, we systematically summarize the research progress of LDH-based photocatalysts in recent years with an overview of utilizing the forceful tunability of LDHs to manipulate sophisticated photocatalytic materials for enhancing solar energy conversion. We shed light onto several typical design principles of LDH-based photocatalysts including component control, defect engineering, hybridization, and derivatization (Scheme 1). Simultaneously, the remaining challenges and future perspectives of LDH-based photocatalysts are also proposed.
2 CONSTRUCTION OF EFFICIENT LDH-BASED PHOTOCATALYSTS

2.1 Component control

Unlike other 2D photocatalytic materials (g-C3N4, BiOX, or black phosphorus), whose component modulation is restricted to a small scope, the exchangeability of cations in layers and anions in the interlayer allows LDHs great flexibility in their composition (Scheme 2), making it feasible to acquire customized electronic structure and active centers for designated photocatalytic reactions by selecting suitable cations and anions facilely. In this section, we elaborated component control strategy of LDH-based photocatalysts for efficient solar spectrum utilization, photogenerated carriers separation and surface catalytic kinetics.

2.1.1 Component control for tunable bandgap

One of bottlenecks for the current research on photocatalytic materials lies in how to broaden the light absorption and enhance solar utilization, as most common semiconductor photocatalysts are just excited by UV light (only 7% of the full spectrum). On the other hand, the positions of valence band (VB) and conduction band (CB) correlate to the redox potentials of photogenerated electron–hole pairs, determining whether the photocatalytic reaction can occur from the thermodynamic point of view. For LDHs, the band position can be regulated by selecting reasonable composition to maximize light utilization. In 2009, the first comprehensive study on ZnM-LDHs (M = Ti4+, Ce4+, and Cr3+) for photocatalytic oxygen evolution reaction (OER) was documented by Hermenegildo Garcia and his coworkers. The conjunction of UV–Vis diffuse reflectance spectra (DRS) and photocatalytic performances in this work unveiled that introduction of Cr3+ can prompt the LDHs strong absorbance and remarkable enhanced photocatalytic OER performance under visible light, which was ascribed to the ligand to metal transitions of Cr-O. Similarly, other MCr-LDHs (M = Cu2+ and Ni2+) were also reported to exhibit absorption peaks at 410 and 570 nm, further suggesting a visible light-responsive photocatalyst. Moreover, different from the comparable metal oxide (NiO or TiO2) whose absorption consists in UV region, CuTi-LDH and NiTi-LDH showed two absorption bands and outstanding apparent quantum yields for OER under visible and near-infrared illumination. The extraordinary light absorption characteristics and powerful photocatalytic performance made investigators realize the broad application prospects of LDHs in photocatalysis, which was distinguished from conventional photocatalysts. Therefore, investigators tried to efficiently predict and screen a series of LDHs through theoretical simulation. Density functional theory (DFT) calculations, as a predominant and efficient means for catalytic materials design on the basis of the semiconductor energy band theory, were used to predict the energy band position of the LDHs with different components. As shown in Figure 1, revealed by computation results using DFT + U method, the band edge position of LDHs can be optionally tuned in a wide range by substituting metal ions in host layers, and the usual anions exchange (CO3, Cl, or NO3) in the interlayer would impact band edge placement slightly. Furthermore, the reaction barriers of OER...
over different LDHs could be acquired by calculating the free-energy change of the four oxidation steps (\(^*\), \(^*\)OH, \(^*\)O, and \(^*\)OOH) for screening possible LDH-based photocatalysts.\(^{34,35}\) Accordingly, a design concept for energy band and light absorption for LDH-based photocatalysts in view of component modulation can be proposed: (1) the introduction of “colored metal” (such as Cu\(^{2+}\), Ni\(^{2+}\), or Cr\(^{3+}\)) can endow as-designed LDHs with the visible-light response; (2) the types of interlayer anions or the ratio of the cations in the host layers can be altered to achieve fine-tuning of the energy band position, which can be adopted for meeting requirements of distinct photocatalytic reactions and reducing the occurrence of side reactions; and (3) computational approaches are predominant and efficient means to predict and screen LDHs with different components for particular reactions, thereby significantly improving the experimental efficiency and cutting the trial and error.

2.1.2 | Component control for charge transfer dynamics

The major obstacle of the unsatisfactory utilization efficiency for photogenerated carriers is fast electron–hole recombination, dramatically limiting the photocatalytic properties of LDH-based photocatalysts.\(^{36}\) To alleviate this problem, investigation of the migration path for photogenerated electrons in LDHs is demanded to provide guidance for the design toward efficient charge transfer dynamics. Two migration paths of photogenerated electrons in LDH crystals: horizontal migration within LDH hydroxide layer and vertical migration between LDH layers. As a comparison, [Cu\((\text{OH})_4\)]\(^{2-}\) inserted ZnGa-LDH and ZnCuGa-LDH with CO\(_3^{2-}\) intercalation were respectively synthesized as photocatalysts for hydrogenation of CO\(_2\). X-ray absorption fine structure (XAFS) spectra were employed to observe the subtle evolution of metal valence in LDHs which can directly mirror the separation and capture of photogenerated carriers.
electrons. Theoretically, the photogenerated electrons can be trapped at the two different Cu sites in LDHs, thereby the operando Cu K-edge X-ray absorption near-edge structure (XANES) spectroscopy under the reaction conditions would be effectual. In Figure 2A, when the photogenerated electrons separated and diffused to the Cu sites under illumination, Cu$^{2+}$ (a pre-edge peak because of a 1s–3d transition) was reduced to Cu$^{+}$ (no pre-edge peak), resulting in decreased peak intensity with the extension of illumination time. The different slopes for the two LDHs corresponding to different positions of Cu sites suggested that the migration rate of photogenerated electrons in the perpendicular direction to interlayer Cu sites was much slower than that in host layers.$^{37,39}$ The detected results are in accordance with other 2D materials. Given this conclusion, suitable interlayer anion or intercalation material with high conductivity can be designated for ameliorated vertical migration between LDH layers, to improve the apparent carriers transfer efficiency of LDHs.

The efficient migration of excited electrons along the horizontal direction in LDH layers is widely believed to benefit from the metal-to-metal charge-transfer (MMCT) mechanism based on bridged bimetallic linkages of M$^{2+}$–O–M$^{3+}$ with adjustability from optimizing the ratio of M$^{2+}$ and M$^{3+}$ in LDHs. Kang et al. reported that CoFe-LDHs with distinguishing Co$^{2+}$/Fe$^{3+}$ ratios displayed varying activities for photocatalytic water oxidation at the sequence of Co$_{2.23}$Fe-LDH > Co$_{3.33}$Fe-LDH > Co$_{4.16}$Fe-LDH. It was attributed to the appropriate proportion of Co–O–Fe bridges in Co$_{2.23}$Fe-LDH that suppressed the fast electron–hole recombination.$^{40}$ Besides, the introduction of metal elements with specific electronic structures into LDH laminates is another means to improve charge transfer dynamics. Lanthanide metal ions, which possess abundant 4f electrons and vacant d-orbitals, are able to adjust the local electronic state and introduce new energy levels. Accordingly, introducing lanthanides ions into the host layers of LDHs can inhibit the charge recombination and increase the charge injection efficiency simultaneously, leading to more efficient charge transfer dynamics. The photoluminescence (PL) behavior and photoelectrochemistry measurements over Tb$^{3+}$ doped ZnCr-LDH demonstrated more efficient separation of photogenerated carriers and higher charge injection efficiency, leading to the duple photocatalytic activity for OER than that of pristine ZnCr-LDH.$^{38}$ Besides, Ce$^{4+}$ doped ZnAl-LDH afforded higher activity for photodegradation of phenol compared with pristine ZnAl-LDH. The essential reason for the enhanced performance was attributed to the presence of Ce element in ZnAl-LDH with different oxidation states (Ce$^{4+}$ and Ce$^{3+}$) that acted as electron or hole acceptors to avoid their recombination.$^{42}$ These studies inspire us that diversified metal components can be introduced into LDH layers for efficient carriers transfer dynamics. One is the metal component with variable

![Figure 2](image-url)
valence state which was contributed to the acceptance and transmission of electrons, the other is a metal site for efficient adsorption of reactant to prompt the injection of photogenerated electrons.

2.1.3 Component control for surface catalytic kinetics

It is widely accepted that the catalytic reaction occurred on catalyst surface and the atom component and electronic structure of photocatalyst surface is directly related to catalytic activity and selectivity. Especially for some photocatalytic micromolecule reactions, specific metal catalytic sites facilitate the substrates adsorption, reducing reaction activation energy and realizing performance and selectivity regulation.43,44 Various transition metals can be introduced into the layer or interlayer of LDHs in the form of metal cations or complex anions,45,46 which provides not only broad space for the directional catalysts' design, but also offer precise photocatalytic sites for study on the surface reaction mechanism.

Taking LDHs for CO2 photoreduction as examples, the reaction rate and selectivity are two essential indexes to evaluate the photocatalyst, which can be optimized by regulating the active sites in LDHs (Table 1). Teramura's group found that O2 could be directly produced from the decomposition of the hydroxyl groups in LDH layers in photocatalysis. Accordingly, the generated rates of CO from CO2 photoreduction could be boosted by tuning the water tolerance of base sites of M2+M3+-LDHs (M2+ = Ni2+, Zn2+ and Mg2+, M3+ = Al3+, Ga3+, and In3+).47 In addition to the yield, the superiority of LDH photocatalysts reflected in their advanced catalytic selectivity which can be achieved by designing the active surface sites of catalysts. Zhang et al. systematically

| Sample       | Reaction medium | Light source       | Reaction rate (μmol g⁻¹ h⁻¹) | Ref. |
|--------------|-----------------|--------------------|-------------------------------|-----|
| NiAl-LDH     | CO2 (500 μL)/H2O (4 mL) | 200 W Hg-Xe lamp  | CO: 1.9                       | 47  |
| NiGa-LDH     | CO2 (500 μL)/H2O (4 mL) | 200 W Hg-Xe lamp  | CO: 3.1                       | 47  |
| NiIn-LDH     | CO2 (500 μL)/H2O (4 mL) | 200 W Hg-Xe lamp  | CO: 3.6                       | 47  |
| MgAl-LDH     | CO2 (500 μL)/H2O (4 mL) | 200 W Hg-Xe lamp  | CO: 2.4                       | 47  |
| MgGa-LDH     | CO2 (500 μL)/H2O (4 mL) | 200 W Hg-Xe lamp  | CO: 2.6                       | 47  |
| MgIn-LDH     | CO2 (500 μL)/H2O (4 mL) | 200 W Hg-Xe lamp  | CO: 1.6                       | 47  |
| ZnAl-LDH     | CO2 (500 μL)/H2O (4 mL) | 200 W Hg-Xe lamp  | CO: 2.4                       | 47  |
| ZnGa-LDH     | CO2 (500 μL)/H2O (4 mL) | 200 W Hg-Xe lamp  | CO: 1.9                       | 47  |
| ZnIn-LDH     | CO2 (500 μL)/H2O (4 mL) | 200 W Hg-Xe lamp  | CO: 0.7                       | 47  |
| ZnTi-LDH     | CO2 (0.08 MPa)/H2O (g) | 300 W Xe lamp     | CH4: 1.2                      | 38  |
|              |                 |                    | H2: 0.7                       |     |
| ZnFe-LDH     | CO2 (0.08 MPa)/H2O (g) | 300 W Xe lamp     | H2: 1.8                       | 38  |
| ZnCo-LDH     | CO2 (0.08 MPa)/H2O (g) | 300 W Xe lamp     | H2: 1.1                       | 38  |
| ZnGa-LDH     | CO2 (0.08 MPa)/H2O (g) | 300 W Xe lamp     | CO: 1.6                       | 38  |
| ZnAl-LDH     | CO2 (0.08 MPa)/H2O (g) | 300 W Xe lamp     | CO: 1.3                       | 38  |
| CoAl-LDH     | CO2 (400 ppm)/H2O (g) | 500 W Xe lamp     | CH4: 4.3                      | 48  |
|              |                 |                    | CO: 0.36                      |     |
| CoAl-LDH     | CO2 (0.18 MPa)/H2O (l) | 300 W Xe lamp (600 nm) | CO: 43730                      | 49a |
|              |                 |                    | H2: 34580                      |     |
| ZnAl-LDH     | CO2 (0.08 MPa)/H2O (g) | 300 W Xe lamp     | CO: 7.6                       | 50  |
| NiAl-LDH     | CO2 (0.18 MPa)/H2O (l) | 300 W Xe lamp (400–800 nm) | CH4: 168                      | 51a |
|              |                 |                    | CO: 712                        |     |
|              |                 |                    | H2: 134                        |     |
| NiCoFe-LDH   | CO2 (0.18 MPa)/H2O (l) | 300 W Xe lamp (400–800 nm) | CH4: 379                      | 52a |
|              |                 |                    | CO: 210                        |     |
|              |                 |                    | H2: 80                         |     |

*Photosensitizer (Ru-(bpy)3Cl2/6H2O) and sacrificial agent (TEOA) were employed in these reaction systems.
examined the photocatalytic CO₂ reduction selectivity for a series of Zn²⁺-containing LDHs (ZnM-LDHs, where M = Al³⁺, Fe³⁺, Co³⁺, Ga³⁺, and Ti⁴⁺) (Figure 2B). After deliberately selecting M metals ions with empty (Ti⁴⁺), half-filled (Fe³⁺, Co³⁺), completely-filled (Ga³⁺), or nonexistent (Al³⁺) d orbits in ZnM-LDHs, different photocatalytic CO₂ reduction selectivity appeared. ZnTi-LDH promoted both CO₂ and H₂O adsorption and conversion, affording CH₄ as the dominant reaction product. ZnGa-LDH and ZnAl-LDH each had a moderate CO₂ adsorption capacity and negligible H₂O adsorption, resulting in the production of CO. Whereas for ZnFe-LDH and ZnCo-LDH, H₂O adsorption was preferred, thus H₂ yielded as the main product (Figure 2C–E). Based on these results, the d band center was introduced as a theoretical descriptor to explain the relationship between the tri/tetravalent cations in the ZnM-LDH photocatalysts and their CO₂ reduction selectivity. The placements of ε₄ that closer to Fermi level, which mainly depended on the property of metal element in LDH, lowered the barrier of electron injection from LDH catalysts to the adsorbates, thereby facilitating the activation to reactive molecules. In addition to the types of elements, the valence of the metal elements in the host layers is another factor to control the photocatalytic selectivity artificially. Wang and coworkers successfully constructed partial trivalent cobalt into CoAl-LDH layers for heterogeneous photocatalytic CO₂ reduction, with the CO yield being superior to that of CoAl-LDH with few trivalent cobalt (H₂ and CH₄ as the main reduction products). The enhanced performance was ascribed to the existence of trivalent cobalt’s weak capability to dissociate H₂O, and then restricted the step that H* reacted with intermediates CO* to generate CH₄.

2.2 | Defect engineering

Apart from intrinsic composition and structure of materials, surface defect sites also play vital roles in photocatalysis: (1) creating defect energy level within the forbidden band to extend the absorption edge; (2) trapping photogenerated carriers to promote carrier separation; and (3) creating active centers for adsorption and activation of reactant. In recent years, defect engineering in LDHs have been widely highlighted, such as oxygen or metal atom vacancy, heteroatom substitution and lattice distortion. In this part, different tailor-made defect constructing strategies with high photocatalytic activity are discussed in detail.

2.2.1 | Constructing defects in LDHs via size effect

Generally, decreasing lateral/longitudinal dimension is an effective and straightforward means to introduce surface defects and boost surface area. Zhang et al. reported that ultrathin defect-rich ZnAl-LDH nanosheets with abundant oxygen vacancies (Vo) were very active for CO₂ photoreduction. As evidenced by XAFS (Figure 3A–D), the coordinatively unsaturated Zn with lower oxidation state was created along with solely distorted octahedral Zn–O coordinative environment in the ultrathin ZnAl-LDH nanosheets. As shown in Figure 3E, the enhanced intensity for electron spin-resonance spectroscopy (ESR) signal further proved the existence and reinforcement of coordinatively unsaturated Zn sites after 20 min of UV–Vis light irradiation. The similar results cannot be observed for that of bulk ZnAl-LDH (Figure 3F). Additionally, relative defect concentration was quantified by positron annihilation spectrometry. The larger relative intensity of the positron lifetime for ultrathin ZnAl-LDH nanosheets assigned to positrons trapped by Zn-Vo indicated the predominance of large-size surface defects. On the basis of experimental results above, DFT calculation further revealed that a new defect level was created within the band gap of defect-rich ZnAl-LDH and the adsorption energy for CO₂ and H₂O were both larger than those of defect-free LDH. Except ZnAl-LDH, NiTi-LDH nanosheets with different lateral sizes were successfully prepared using a reverse microemulsion method for photocatalytic OER by Wei and coworkers. With lateral sizes of nanosheets decreasing from 90 to 30 nm, gradually increasing densities of Ti³⁺ defects were gotten, resulting in elevated activities from 5.86 to 13.45 μmol m⁻² h⁻¹. Besides, it was reported that the relative concentration of defects in NiAl-LDH varied with the numbers of layers in the rank of b-NiAl-LDH (27 nm, multiple layers) < f-NiAl-LDH (5 nm, few layers) < m-NiAl-LDH (1 nm monolayer). Interestingly, there were two types of surface defects in m-NiAl-LDH: metal vacancies (V₅₆(M = Ni or Al) and hydroxyl vacancies (V₉₄). As shown in Figure 3G,H, the CH₄ evaluated rates increased and H₂ evolution reaction (HER) was suppressed when the thickness decreased. Furthermore, HER over m-NiAl-LDH was completely suppressed under irradiation with λ > 600 nm (Figure 3H). DFT calculation (Figure 3I) explained that photogenerated electrons tended to transfer to the defect state under irradiation above 600 nm, and the driving force corresponding to the defect level could overcome the potential barrier for CO₂ methanation, but not enough to drive H₂ evolution. It follows that LDHs are comparatively ideal model materials for further study on the role of defects on photocatalysis, benefiting from their controllable synthesis, adjustable size and thickness. Moreover, a series of advanced characterization techniques are imperative for the analysis and understanding of defect structures from multiple aspects, including crystal structure and electronic structure.
Size effect can not only induce the formation of atomic vacancy defect, varying degrees of distortion or strain will also form in crystal structure in order to decrease the system energy, further modulating electronic structure of catalysts, which can be utilized to develop efficient photocatalysts as well.\(^{58,59}\) It was reported that tensile strain was introduced into NiFe-LDH via mechanical ball-milling, which facilitated oxygenated intermediates adsorption for efficient electrocatalytic OER.\(^{60}\) Moreover, strain engineering was also utilized to regulate LDH nanosheets for visible-light-driven nitrogen reduction reaction (NRR).\(^{61}\) The diffraction peaks ascribed to (110) facets in X-ray powder diffraction (XRD) patterns for both ultrathin CuCr-LDH nanosheets and ZnAl-LDH nanosheets shifted to higher angles compared with the corresponding bulk LDH respectively, suggesting abundant Vo caused severely distorted structure and in-plane biaxial compressive strain in the (110) plane. Addition of compressive strain in CuCr-LDH created defect levels within the bandgap, which served as electron-trapping sites to facilitate electron transfer to chemisorbed N\(_2\) molecules. Besides, the presence of strain in CuCr-LDH increased adsorption energy for N\(_2\) and weakened the N-N triple bond compared with pristine CuCr-LDH sample or strain-free CuCr-LDH-Vo, achieving efficient adsorption and activation of N\(_2\) for enhanced NH\(_3\) production rate.

2.2.2 Constructing defects in LDHs via doping strategy

Doping is one of the most common methods to construct defects. When metal heteroatoms are doped into the LDH
lattice, the mismatch between the heteroatoms and the original lattice sites will lead to the loss of oxygen atoms, generating exposed metal sites with unsaturated coordination (M-Vo sites, Figure 4A) as active sites for photocatalytic reactions. Very recently, our group reported the synthesis of defect-rich ZnAl-LDH with Vo and coordination unsaturated Cu⁵⁺ (δ < 2) via a facile doping strategy. The defected structure was determined by the studies of X-ray absorption spectra (XAS), X-ray photoelectron spectroscopy (XPS) (Figure 4B), and Auger electron spectroscopy. Theoretical computations results revealed the presence of electron-rich Cu⁵⁺ (δ < 2) centers through the analysis of Bader charge of the Cu⁵⁺ and charge density difference (Figure 4C). The electron-rich Cu⁵⁺ and surrounding Vo conferred ZnAl-LDH robust ability for charge separation/injection and N₂ adsorption/activation, thereby leading to efficient photocatalytic nitrogen fixation into NH₃ (110 μmol g⁻¹ h⁻¹ for 5% Cu⁵⁺ doped ZnAl-LDH, compared with 17.1 μmol g⁻¹ h⁻¹ for pristine ZnAl-LDH).

Similarly, when Ni²⁺ was introduced into CoFe-LDH, multi-vacancies were created. PL spectroscopy, photocurrent, and electrochemical impedance spectroscopy (EIS) measurements evidenced that Vo and metal vacancies in LDH nanosheets enhanced the separation and mobility efficiency of photogenerated carriers. Dong et al. demonstrated the partial substitution of Mg²⁺ by Ni²⁺ in MgAl-LDH nanosheets signally ameliorated their photocatalytic activity for NO removing. Ni²⁺ doping led to the increased light absorption and red-shifted absorption edge, observed from UV–Vis DRS spectra. Experimental and computational results unveiled this phenomenon (Figure 4D,E): (i) Ni²⁺ elevated both the CB and VB positions; and (ii) the presence of oxygen vacancy upshifted VB, introduced a defect energy level within the band gap and downshifted the CB position. In addition, Vo sites were beneficial to H₂O molecule adsorption, which promoted Ni/LDH to produce ·OH radicals for oxidizing NO even under a low partial pressure. Inspired by this, doping univalent metal ions (e.g., Cu⁺ or Ag⁺) or easily reduced high-valence metal ions (e.g., Ni³⁺, Co³⁺ or Mn⁴⁺, followed by a gentle reduction step) into LDH host layer, which tends to induce loss of lattice oxygen, is promising to generate M-Vo active sites for photocatalysis.

2.2.3 | Constructing defects in LDHs via etching

Intentional damage to crystal structure is a direct way to create defects, such as etching materials by physical or chemical means to remove part of the component atoms,
leaving behind porous structures and vacancies. Wang's group reported a simple approach to etch CoFe-LDH via an acid–base reaction, where HNO₃ was used as etching agent utilizing intrinsic alkalinity of LDHs (Figure 5A). As a result, CoFe-LDH was exfoliated and created multiple atomic vacancies. In addition, plasma treatment of LDHs could not only weaken the electrostatic interactions between host layers and interlayer cations, but also destroy the covalent bonds in host layers in the lateral direction. When bulk CoFe-LDH was etched by water plasma or Ar plasma, exfoliated ultrathin nanosheets with multiple vacancies (including O, Co, and Fe vacancies) were formed (Figure 5B). Obviously, the plasma treatment strategy is universal for defected LDHs design.

Actually, the etching effect by acid or plasma usually acts on the entire LDH structure, leading to the simultaneous formation of multiple defects. Thus, the improved catalytic performance of the obtained defective catalysts originated from the co-contribution of multiple defects. Sun and coworkers deliberately introduced amphoteric Zn²⁺ or Al³⁺ sites into NiFe-LDH, obtaining NiFeAl-LDH or ZnNiFe-LDH. Then, the Zn²⁺ or Al³⁺ sites were selectively etched by KOH solution in order to expose unsaturated O-coordination divalent metal or trivalent metal sites for catalytic reactions. Taking inspiration from Sun’s work, Zhang et al. used alkaline etching strategy to synthesize a series of defect-rich LDH nanosheet photocatalysts (including ZnCr-LDH, ZnAl-LDH, and NiAl-LDH) for N₂ photofixation to NH₃ in pure water under ambient conditions. Among those, as-prepared defective ZnCr-LDH exhibited superior activity relative to the pristine ZnCr-LDH (NH₃ evolution rate was ~33.19 μmol g⁻¹ h⁻¹ under UV–Vis illumination, with a quantum yield of ~0.11% at 550 nm which was 10 times as high as that of pristine ZnCr-LDH under the same testing conditions). The etching degree was tuned by controlling the duration of alkali treatment. Figure 5C,D showed that unsaturated Zn sites could be effortlessly generated during the etching process and the Gibbs free energy for hydrogenation of N₂ stepped down after the introduction of zinc vacancies. The experimental results showed that the amount of zinc element in ZnCr-LDH nanosheets

**FIGURE 5** (A) Scheme showing the process of acid etching LDH. Reproduced with permission from Reference 65. Copyright 2017, Royal Society of Chemistry. (B) Schematic illustration of the water-plasma-enabled exfoliation of CoFe-LDH nanosheets. Reproduced with permission from Reference 66. Copyright 2017, Wiley-VCH. (C) DFT predicted activity for N₂ adsorption and hydrogenation on different types of ZnCr-LDH surfaces (containing saturated or unsaturated Zn sites). (D) Formation energy of Vo in defect-free ZnCr-LDH and ZnCr-LDH with zinc vacancies. Reproduced with permission from Reference 67. Copyright 2020, Wiley-VCH
diminished gradually during the etching process, resulting in numerous Vo and metal vacancies, as well as coordinatively unsaturated metal sites. The universal synthesis strategy could be successfully extended to synthesiz other defective materials and similarly improve their performance for N2 photoreduction to NH3 or other photocatalytic reactions.67

2.3 Hybridization design of LDH-based materials

Hybrid materials act as an indispensable role in the family of photocatalysts. In detail, combining two semiconductors with matching energy band to construct a heterojunction, internal electric field or Z-scheme is a common approach to expand the absorption spectrum and facilitate carriers separation, for enhanced photocatalytic reaction efficiency.70 Additionally, compositing LDHs with other semiconductors can introduce new active sites for lowering the activation energy barrier for different reactions, such as water splitting, CO2 photoreduction, N2 photofixation.21–73 The intercalation structure and various synthesis methods enable LDHs to construct hybrids with a variety of materials.

For structural design, several interactions (covalent bond, electrostatic force, and Van der Waals' force) can bond, electrostatic force, and Van der Waals' force) can be utilized to provide multiple combination modes for the construction of LDH-based composites, realizing efficient separation and transfer of photogenerated carriers. Positively charged host layers allow LDHs to self-assemble with negatively charged species by electrostatic interaction,74 which facilitates the transfer of electrons through interface, resulting in enhanced carrier separation efficiency. Hwang's group reported the fabrication of several self-assembled nanohybrids via the electrostatic interaction, selecting exfoliated ZnCr-LDH as photosensitizer and active catalytic site, and electronegative two-dimensional materials (titanate75 and graphene oxide76) or polyoxometalate cluster77 with suitable band position as photogenerated electron acceptor. The mesoporous layer-by-layer ordered structure was observed clearly by high-resolution transmission electron microscope (HRTEM) as shown in Figure 6A. The close contact and strong interaction between two phases could effectively promote the migration of photogenerated electrons from LDHs to the electron acceptor, and then realize the effective separation of electrons and holes, thereby obtaining higher photocatalytic OER activity compared with that of pure ZnCr-LDH. This obtained results demonstrated that the electrostatic interaction was very effective to obtain the close-contact LDH self-assemblies with improved charge carrier separation. More direct evidence about electron transfer and interaction between LDHs and the other component were gotten by Zhou and his coworkers.78 As shown in Figure 6B,C, a homoheterojunction consisting of ZnCr-LDH nanosheets and electronegative BiOCl nanoplates was constructed via electrostatic interaction. In situ Kelvin probe force microscopy (KPFM) and surface photovoltage microscopy (SPVM) experiments were performed to detect the energy band alignment and charge transfer in homoheterojunction between BiOCl and ZnCr-LDH. After combining with LDH, the increased surface potential signals suggested a downward band bending formed at the interface between BiOCl and LDH, which offered force to drive the photogenerated electrons transfer from BiOCl to LDH (Figure 6D). The SPV signals negatively shifted after stacking ZnCr-LDH onto the BiOCl nanoplate. This directly proved that the photogenerated electrons migrated from BiOCl to ZnCr-LDH across the built-in electric field at interface (Figure 6E). The advanced in situ techniques (KPFM and SPVM) offer visual evidence to the study of electron migration and interfacial electric fields in LDH composite photocatalysts.

The photocatalytic performance of composite materials is closely related to their preparation methods. LDH crystals nucleate and grow easily when metal salt solution and alkali solution are mixed in a certain range of pH,79 which allows LDHs to be combined with a variety of materials at very moderate conditions without destroying their intrinsic structure and function.80 Some typical semiconductor photocatalysts, such as TiO2 and Cu2O, were frequently used as nucleation centers for LDHs' vertical growth in the synthesis process to construct a heterojunction for improving photocatalytic activity.81,82 For well-studied TiO2/NiAl-LDH composite photocatalyst in which the NiAl-LDH in situ vertically grew on TiO2 hollow nanospheres (Figure 7A), XPS spectra showed that the peaks assigned to Ti in TiO2 shifted negatively and the peaks assigned to Ni in NiAl-LDH shifted positively after composited (Figure 7B), suggesting a significant interaction between TiO2 and NiAl-LDH which facilitated photoinduced charge separation for enhanced CO2 reduction activity. Extension of absorption spectrum and improved carrier separation efficiency were demonstrated respectively by UV–Vis DRS and PL analysis.83 Similarly, ZnO nanowires covered with NiCo-LDH nanoflakes were prepared to boost photoelectrochemical activity by using a facile electrolysis under the alkaline environment (another effective means to control the LDHs growth).85 Meanwhile, Cu2O with matching energy bands was often employed to composite with LDHs to form a Z-scheme photocatalyst because of its considerable activity for water splitting or CO2 photoreduction (Figure 7C). An ingenious synthesis method can
FIGURE 6 (A) Cross-sectional HRTEM image of the layered titanate/ZnCr-LDH nanohybrid and its enlarged view and structural model. Reproduced with permission from Reference 75. Copyright 2011, American Chemical Society. (B) Band edge positions for BiOCl and ZnCr-LDH and the charge transfer between them. (C) HRTEM image of the standing BiOCl/ZnCr-LDH. (D) Histogram of the mean of CPD signals collected from some randomly selected particles. Insert: proposed band alignment between BiOCl and ZnCr-LDH. (E) Histogram of the mean of SPV signals collected from randomly selected some particles. Reproduced with permission from Reference 78. Copyright 2018, Royal Society of Chemistry.

FIGURE 7 (A) Transmission electron microscope micrographs of the TiO2/LDH core-shell hybrid. (B) High-resolution XPS spectra of the TiO2, LDH, and TiO2/LDH core-shell hybrid sample. Reproduced with permission from Reference 83. Copyright 2020, Royal Society of Chemistry. (C) Schematic illustration for the photoexcited electron separation/transport in the Cu2O@ZnCr-LDH system. (D) Schematic illustration for the preparation of Cu2O@ZnCr-LDH hollow core-shell photocatalyst. (E) Schematic illustration for the interface of Cu2O@ZnCr-LDH (S2O3 − intercalated) structure. Reproduced with permission from Reference 84. Copyright 2017, Elsevier.
optimize the hybrid of Cu2O with LDHs to achieve a stable composite structure for efficient interface electron transfer. Some kinds of interlayer anions in LDHs can form chemical bond with metal oxides, and this interaction has been utilized to prepare efficient LDH-based composite photocatalysts. ZnCr-LDH nanoplates anchored on hollow Cu2O nanocubes were synthesized using Cu2O nanocubes as soft template. During the preparation process, as shown in Figure 7D, S2O32−, one typical interlayer anion in LDHs, was chosen as soft base for an inwards etching of cubic Cu2O to release OH− anion. Then, the OH− reacted with Zn2+ and Cr3+ to generate ZnCr-LDH with S2O32− as interlayer anion on the surface of hollow Cu2O. Importantly, the chemical bonding formed between Cu2O and S2O32− in ZnCr-LDH played a vital role in optimizing the heterojunction interface (Figure 7E). Due to the formation of optimized heterojunction interface, Cu2O@ZnCr-LDH exhibited excellent activity for photocatalytic pure water splitting (0.90 and 0.44 μmol h−1 for H2 and O2), superior to that of pristine Cu2O nanocubes (0.32 and 0.14 μmol h−1) and ZnCr-LDH (trace).84 Katsumata and his coworkers prepared a series of Cu2O-loaded ZnCr-LDHs utilizing ZnCr-LDHs and ascorbic acid as a precursor and weak reductant for in situ reduction of Cu2+ in LDH laminates to produce Cu2O.86 Recently, Zhang’s group reported a facile synthesis of ultrafine Cu2O with an average lateral size of below 3 nm loaded LDHs via this in situ reduction strategy for nitrogen photoreduction. The optimized Cu2O-LDH exhibited remarkable 23-fold higher activity for visible-light-driven reduction of N2 to NH3 in pure water (NH3 production rate = 30.31 μmol g−1 h−1) than bulk Cu2O-LDH (NH3 production rate = 1.29 μmol g−1 h−1). Electrochemical measurements revealed positively shifting onset potential and enhanced current density for N2 reduction over ultrafine Cu2O compared with the bulk Cu2O, indicating that the supported ultrafine Cu2O lowered the N2 activation barrier. This simple and efficient method represents a promising future strategy for developing and designing LDH-based photocatalysts.87

2.4 Topological transformation of LDHs to derivants

Not only LDHs themselves can act as photocatalysts but a variety of MMO, hybrid of metal and metal oxide, alloys, nitrides, sulfides, and phosphides derived from topological transformation of LDHs at different temperature and atmosphere, which cannot be easily obtained by conventional synthesis methods, also exhibit extraordinary photocatalytic performance mainly benefiting from structural advantages of the precursor LDHs,88 elaborated below in detail. (1) The ordered distribution of metal cations in the LDH laminates ensures the structural homogeneity of the derivants. ZnₓCd_{1−x}S solid-solution nanoparticles which were synthesized by calcination of ZnCdAl-LDH precursor in H2S atmosphere exhibited much better photodegradation performance of methylene blue than ZnₓCd_{1−x}S photocatalysts obtained by the conventional co-precipitation method or calcination of the ZnAl-LDH/CdAl-LDH mixture. The enhanced photocatalytic activity was attributed to the homogeneous structure of the solid-solution ZnₓCd_{1−x}S that can inhibit the recombination of photogenerated carriers.89 (2) Easily controlled metal cation component in the LDH laminates determines very rich composition of the final derivants. (GaN)_{1−x}(ZnO)ₓ solid solutions were prepared by thermal treatment of ZnGa-LDH under NH3 flow and used for efficient photoreduction of Cr6+ ions. The tailor-made proportion of ZnO and tunable band gap of (GaN)_{1−x}(ZnO)ₓ were achieved just by facilely controlling the Zn/Ga ratio in the LDH precursors, which was superior to the traditional synthetic method.90 (3) The intercalation structure of LDHs makes elemental doping more uniform. The interspace between LDH layers benefits for the diffusion of gaseous dopant sources (NH3, H2S, etc.). In addition, organic molecules can be directly intercalated between the periodic layers as nitrogen or carbon source, so that uniform doping can be obtained after the in situ structural transformation. For instance, after terephthalate-intercalated ZnAl-LDH was annealed under NH3 flow, nanostructured MMO co-doped by carbon and nitrogen atoms uniformly were obtained, originating from the presence of interlayer interspace and intercalated ordered terephthalate.91

In addition to the above-mentioned solid solutions or doped structures, heterostructures with unique heterojunction interfaces can be obtained from LDHs via a typical topological transformation process. The heterojunction interface of LDH derivants plays a very critical role in improving their photocatalytic performance by separating photoinduced charge carriers efficiently or directly acting as active site for photocatalytic reactions. Through a heated dehydration process, LDHs can be converted into MMO controllably with a large number of high-quality heterojunction interfaces. A detailed study on the topological transformation of ZnCo-LDH found that abundant interfaces were formed between Co3O4 and ZnO phases containing coexistence of Zn-doped Co3O4 and Co-doped ZnO demonstrated by XRD, HRTEM and XAFS. With calcination temperature increased, the heterojunction interfaces between crystal grains became more evident,92 while the amount of the heterojunction interfaces diminished as the size of crystal grains increased. Al3+-containing LDHs have been frequently utilized as precursors for the preparation of
nanostructured MMO, hybrids of metal and metal oxide, and metal alloys uniformly dispersed on inert Al2O3 support with abundant heterojunction interfaces for efficient photocatalytic performance by the in situ topological transformation.93-97 Zhang's group reported that nickel nanoparticles decorated with discrete NiOx (Ni-525) were prepared via hydrogen reduction of NiAl-LDH at a specific temperature, which were characterized by XAFS and HRTEM (Figure 8A–D). The NiOx overlayer was proved to modulate the electronic structure of metallic Ni nanoparticles. The unique Ni/NiOx interface structure caused a higher barrier for *CH3 hydrogenation to CH4 and lowered C–C coupling barrier, leading to the high-selectivity higher hydrocarbons under visible irradiation.98 In addition, Fe-based heterostructured photocatalysts were also fabricated via reducing ZnFeAl-LDH in hydrogen atmosphere and employed for visible light-driven CO hydrogenation. As shown in Figure 8E, with the increase of reduction temperature, FeOx/ZnO, Fe/FeZnOx, FeZn alloy were prepared respectively. The heterostructured nanoparticles obtained at 500 °C consist of Fe0 and FeOx supported on ZnO and amorphous Al2O3, exhibiting high photocatalytic alkenes selectivity for CO hydrogenation, with suppressed water gas shift activity to CO2. The theoretical calculations suggested that the interfaces between metallic Fe and oxides (Figure 8F), and the photoinduced excited state (Figure 8G) together contribute to the selective

![Figure 8](image-url)
conversion of CO and H₂ to olefins and low CO₂ selectivity. ⁹⁹ Theoretically, metals (such as Cu or In) with powerful localized surface plasmon resonance (LSPR) effect also can be introduced into LDH precursors to synthesize the antenna-reactor composites comprising of LSPR active metal and active catalytic center (in the form of alloy or dimer structure) with excellent photocatalytic performance. The above schemes enlighten us in the design of LDH derivants for efficient photocatalysis in the future.

### 3 CONCLUSIONS AND PERSPECTIVES

Herein, we have summarized the strategies for optimizing the catalytic performance of LDH-based photocatalysts from four aspects: component control, defect engineering, hybridization, and topological transformation. Tailor-made materials design and fabrication are integrated with comprehensive characterization methods to elucidate the overall structure-performance correlations, which provided a systematic and in-depth understanding of LDH-based photocatalysts. Over the past decade, the studies on LDH-based photocatalytic materials have shifted from composition/morphology control to precise tailoring of materials properties at atomic scale. The performances of some LDH-based photocatalysts for water splitting and nitrogen fixation are summarized in Table 2. In spite of the rapid development of LDH-based photocatalysts for solar fuels production, there are still a number of bottlenecks to be overcome urgently for a step-change improvement in their photocatalytic performance.

### Table 2 Summary of various LDH-based photocatalysts for photocatalytic water splitting and nitrogen fixation

| Sample           | Light source                  | Reaction | Sacrificial agent | Catalytic activity (μmol g⁻¹ h⁻¹) | Ref. |
|------------------|-------------------------------|----------|-------------------|-----------------------------------|------|
| ZnCe-LDH         | 200 W Xe-Hg lamp (>400 nm)    | OER      | AgNO₃             | O₂: 626                           | 27   |
| ZnTi-LDH         | 200 W Xe-Hg lamp (>400 nm)    | OER      | AgNO₃             | O₂: 268                           | 27   |
| ZnCr-LDH         | 200 W Xe-Hg lamp (>400 nm)    | OER      | AgNO₃             | O₂: 1073                          | 27   |
| NiTi-LDH         | 300 W Xe lamp (400–700 nm)    | OER      | AgNO₃             | O₂: 49                            | 31   |
| CuTi-LDH         | 300 W Xe lamp (400–700 nm)    | OER      | AgNO₃             | O₂: 31                            | 31   |
| ZnTi-LDH/Pt      | 300 W Xe lamp                 | HER      | Lactic acid       | H₂: 314                           | 32   |
| NiTi-LDH/Pt      | 300 W Xe lamp                 | HER      | Lactic acid       | H₂: 153                           | 32   |
| MgAlTi-LDH/Pt    | 300 W Xe lamp                 | HER      | Lactic acid       | H₂: 49                            | 32   |
| CoFe-LDH         | 300 W Xe lamp (400–700 nm)    | OER      | AgNO₃             | O₂: 300                           | 40   |
| Tb-ZnCr-LDH      | 150 W Xe lamp (>420 nm)       | OER      | AgNO₃             | O₂: 1022                          | 41   |
| NiTi-LDH         | 300 W Xe lamp (>400 nm)       | OER      | AgNO₃             | O₂: 2148                          | 57   |
| CdS/ZnCr-LDH     | 450 W Xe lamp (>420 nm)       | HER      | Na₂S/Na₂SO₃       | H₂: 1560                          | 72   |
| ZnCr-LDH/titanate| 450 W Xe lamp (>420 nm)       | OER      | AgNO₃             | O₂: 667                           | 75   |
| ZnCr-LDH/RGO     | 450 W Xe lamp (>420 nm)       | OER      | AgNO₃             | O₂: 1200                          | 76   |
| TiO₂/CoAl-LDH    | 300 W Xe lamp (>420 nm)       | OER      | AgNO₃             | O₂: 2240                          | 82   |
| Cu₂O/ZnCr-LDH    | 300 W Xe lamp (400 nm)        | HER      | No                | H₂: 45                            | 84   |
| CuCr-LDH         | 300 W Xe lamp (>400 nm)       | NRR      | No                | NH₃: 57.1                         | 61   |
| NiCr-LDH         | 300 W Xe lamp (>400 nm)       | NRR      | No                | NH₃: 16.8                         | 61   |
| ZnCr-LDH         | 300 W Xe lamp (>400 nm)       | NRR      | No                | NH₃: 6.6                          | 61   |
| NiAl-LDH         | 300 W Xe lamp (>400 nm)       | NRR      | No                | NH₃: 8.0                          | 61   |
| ZnAl-LDH         | 300 W Xe lamp                 | NRR      | No                | NH₃: 15.3                         | 61   |
| 0.5%-CuZnAl-LDH  | 300 W Xe lamp                 | NRR      | No                | NH₃: 110                          | 62   |
| Etched ZnCr-LDH  | 300 W Xe lamp                 | NRR      | No                | NH₃: 33.2                         | 67   |
| Etched ZnAl-LDH  | 300 W Xe lamp                 | NRR      | No                | NH₃: 25.8                         | 67   |
| Etched NiAl-LDH  | 300 W Xe lamp                 | NRR      | No                | NH₃: 29.3                         | 67   |
| Cu₂O/CuZnAl-LDH  | 300 W Xe lamp (400 nm)        | NRR      | No                | NH₃: 30.3                         | 87   |
photocatalysts, such as TiO$_2$\textsuperscript{100}, BiVO$_4$\textsuperscript{101} and carbon nitride\textsuperscript{102}. However, the experimental synthesis of LDHs with a single crystal or high-crystallinity structure is still a challenge. Therefore, an advanced technique is urgently developed to synthesize LDHs with preferentially exposed crystal facets that can provide ideal models to better understand the migration pathways and kinetics of photogenerated carriers, which is of great significance for the study of LDH-based photocatalysts. The construction of facet heterojunction structure may lead to the different migration paths of photogenerated electrons and holes, realizing efficient separation of photogenerated carriers spatially. Moreover, the controllable synthesis of high-energy faceted LDH nanosheets is more conducive to the adsorption and activation of reactants.

2. The photophysical property and structure-performance relationship of some LDH-based photocatalysts requires to be comprehensively understood and elucidated. There are still some many knowledge gaps among the absorption of light responsive LDHs, photogenerated charge transfer process (within or between the LDH laminates), and reactants-LDH surface interaction. A precise and insightful understanding in this regard is extremely important. By virtue of advanced and valid spectroscopic technologies (synchronous illumination XPS and time-resolved absorption spectroscopy) and theoretical simulations (time-dependent density functional theory), charge dynamics within photocatalysts could be preliminarily identified and their roles for catalytic performance improvement could be proposed. Furthermore, advanced series of operando characterization techniques, such as in situ diffuse reflectance infrared Fourier transformation spectroscopy, in situ XPS, and in situ XAFS, are favorable means to capture reaction intermediates or monitor surface properties under the conditions close to real reaction, which are thus crucial to reveal the surface reaction mechanism and decipher structure-performance relationship.

3. Defect engineering strategies in LDH-based nanomaterials reported to date focused on the design and construction of Vo. Few studies on metal vacancies or metal-oxygen vacancies in LDH-based photocatalysts have been reported and more attention are needed. In addition, considering the diversity and wide-ranging functions of defect structures in enhancing photocatalytic performance, establishing advanced characterizations and new methods for qualitative and accurately quantitative analysis of defects is crucially important\textsuperscript{103}

4. Direct calcination at specific temperature and atmosphere is the primary method for the preparation of most LDH derived photocatalysts. Optimizing topological transformation process to realize the rational design of LDH derivants with unique interface structure and defect structure for remarkable photocatalytic performance, deserves a more in-depth investigation. Further, optimizing the transformation process to realize a large proportion of exposure of specific active sites or crystal facets needs more efforts. In order to achieve this goal, some metal elements (e.g., Mn, Mg and Al) can be introduced into LDH precursors as structure promoters during the in situ topological transformation\textsuperscript{104, 105}. In addition, rapid heating modes (i.e., microwave or photothermal heating) or temperature gradient method also can be employed to regulate the transformation process\textsuperscript{106}

5. For many photocatalytic reactions, the rate-determining step is dominated by mass transfer and reactants diffusion prior to the surface adsorption/activation steps. For instance, photocatalytic N$_2$ (g) + H$_2$O (l) and CO$_2$ (g) + H$_2$O (l) involving three phases in both systems, the effective supply of gaseous reactants is severely restricted because of the super hydrophilic surface of LDHs which is not conducive to contact with hydrophobic gaseous reactants. Surface modification or 3D structure construction at the micro/nano scale could be a feasible approach to regulate the surface wettability of LDH-based photocatalysts, realizing the rapid supply of gaseous and liquid reactant simultaneously\textsuperscript{107}. Seeking new strategies to facilely adjust surface wettability of catalysts would be an emerging research hotspot in photocatalysis.

Excellent tunability, low manufacturing cost and efficient catalytic performance endow LDH-based photocatalysts with broad application prospects. With the rapid development of basic and industrial research, their photocatalytic performances are expected to be further improved and get closer to or meet the industrial demand. In the near future, they will be likely to play a non-substitutable role in photo/photothermal catalysis.

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CONFLICT OF INTEREST
The authors declare no conflict of interest.

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