Review Article

Hao Sun, Young-Jung Heo, Ji-Hye Park, Kyong Yop Rhee*, and Soo-Jin Park*

Advances in layered double hydroxide-based ternary nanocomposites for photocatalysis of contaminants in water

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Abstract: Recently, photocatalysis technology has been widely considered as an effective method for solving environmental pollution issues and addressing the energy crisis. Hybrids of layered double hydroxide (LDH) exhibit excellent photocatalytic properties for use in the field of wastewater treatment due to the large interlayer spaces, chemical stability, and low cost. However, pristine LDH suffers from numerous limitations, such as insufficient visible light utilization and a high recombination rate of electron–hole pairs, resulting in degradation of photocatalytic performance. Recent advancements have demonstrated that LDH-based hybrids are suitable nanocomposites for photocatalytic applications when combining LDH with other semiconductors. This article summarizes the progress in the field of LDH-based ternary composites with emphasis on the removal of organic pollutants and heavy metal ions from aqueous media. Moreover, the applications and synthesis of LDH-based ternary composites, including corresponding examples, are discussed. In addition, the interaction mechanisms between photocatalysts and contaminants in water are comprehensively explained. Finally, the review provides insights into the challenges and prospects for the advancement of LDH-based photocatalysts.

Keywords: LDH-based ternary composite, photocatalysis, wastewater treatment

*** Corresponding author: Kyong Yop Rhee,** Department of Mechanical Engineering, College of Engineering, Kyung Hee University, Yongin 17104, Republic of Korea, e-mail: rheeky@khu.ac.kr
*** Corresponding author: Soo-Jin Park,** Department of Chemistry, Inha University, 100 Inharo, Incheon 22212, Republic of Korea, e-mail: sjpark@inha.ac.kr, tel: +82 32 876 7234; fax: +82 32 867 5604
Hao Sun, Young-Jung Heo, Ji-Hye Park: Department of Chemistry, Inha University, 100 Inharo, Incheon 22212, Republic of Korea

1 Introduction

With the gradual progression in modern industrialization and urbanization, water pollution has been attracting global attention as a major environmental problem [1–6]. Thus, eco-friendly and sustainable technologies are urgently required to deal with this issue. Photocatalysis takes advantage of renewable solar energy to realize the degradation of pollutants, such as heavy metals and organic compounds, in water and has been widely regarded as the most appealing solution [7–14]. Photocatalyst plays an important role in solar light harvesting and energy conversion [15–18].

To date, considerable effort has been made in exploring various visible-light-driven materials for photocatalytic applications [19,20]. Among them, layered double hydroxides (LDHs) were recognized as high-efficiency photocatalysts for the degradation of pollutants under visible light [21–26]. LDHs are a type of two-dimensional (2D) material with a hydrotalcite crystal structure that consists of positively charged metal hydroxide layers and intercalated anions. The general formula of LDH is described as $[M_{(1-x)}{}^{2+}M_{(x)}{}^{3+}(OH)_2]^{x+}(A_{x/n})^{n-}{\cdot}mH_2O$, where M^{2+} and M^{3+} are the fraction of bivalent (Mg^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}) and trivalent (Al^{3+}, Fe^{3+}, Ti^{3+}, Cr^{3+}) cations, respectively, A^{n-} represents the interlayer anions, and x represents the molar ratio of trivalent cations to total cation content [27–31]. LDHs have been extensively employed in adsorbents, photocatalysts, H_2O splitting, and many other fields on account of their unique features such as simple preparation, chemical and physical stability, and adjustable composition [32–36]. The most inherent LDH property is exchangeable intercalation, which imparts high catalytic efficiency [37,38]. Nevertheless, the photocatalytic activity of pure LDHs is insufficient due to their low efficiency in utilizing visible light and the rapid recombination of electron–hole pairs [39,40]. As a result, the hybridization of LDHs with various functional groups has been developed to overcome these limitations. This is important because an LDH-based material not only achieves quick separation of charge carriers but also improves solar light absorption [41–43]. Hence, various attempts, including doping with extraneous elements, modifying surface

morphology, and constructing heterojunctions, have been suggested to improve the poor photocatalytic characteristics of these materials [44–48]. Constructing a heterostructure composite system can accelerate charge transfer, while creating redox reaction sites, and has emerged as an effective strategy for improving the photocatalytic activity of composites used in environmental remediation [49–52]. The hybrid nanocomposites of LDH with other semiconductors, specifically LDH-based ternary nanomaterials, have invoked extensive research [53,54]. For instance, Nayak and Parida [55] developed $Ag@Ag_3PO_4/g\text{-}C_3N_4/NiFe\text{-}LDH$ ternary photocatalysts that exhibit great potential for photocatalytic activity compared to binary semiconductor materials. Furthermore, Mureseanu *et al.* [56] synthesized $g\text{-}C_3N_4/LDH/CuONP$ hybrid nanocomposites that significantly enhance visible-light photocatalytic activity due to the suppression of charge recombination and improvement of interfacial contact. However, review articles on the synthesis and applications of LDH-based ternary photocatalysts are seldom published.

In this article, recent research into LDH-based ternary nanocomposites and their potential applications in wastewater treatment is discussed. To the best of our knowledge, this is the first review of the research developments in the field of LDH-based ternary photocatalytic composites. Finally, some stimulating viewpoints on the current situation and prospects are proposed, which may further improve the understanding and extensive application of LDH-based ternary nanocomposites.

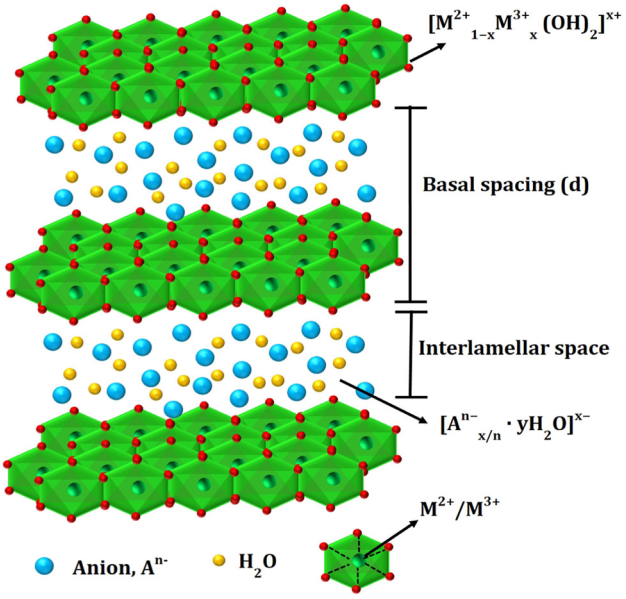

Figure 1: Structure of an LDH. Reproduced with permission from ref. [50]; copyright (2018), Elsevier.

2 Properties and synthesis of LDHs

2.1 Properties of LDHs

LDHs are a type of layered 2D nanostructure, known as hydrotalcite, which is composed of positively charged laminates and negatively charged interlayer anions [57–60], as shown in Figure 1. The surface area of LDHs ranges from 20 to 120 $m^2\,g^{-1}$, providing abundant active sites and excellent photocatalytic performance. Moreover, the absorption capacity of LDHs is significantly improved by heating to 400–600°C [61–64]. The layered crystalline structure of LDHs makes these materials a suitable photocatalyst for combination with other semiconductors. Besides, due to their structure and surface properties, LDHs have been considered as potential absorbent materials for the removal of aqueous pollutants [65–67]. LDHs also provide abundant sites for chemical reactions as heterogeneous solid-base catalysts. LDHs possess many excellent features, such as high chemical stability, distribution of metal cations, biocompatibility, and exchangeable interlayer anions, which are broadly considered as characteristics of remarkable photocatalysts [68,69]. Among them, a significant characteristic of LDH is the exchangeability of interlayer anions, which enables anions to insert into the lamellar spaces of LDHs during synthesis or anionic exchange [70–75]. Moreover, the cationic interlayer structure can accommodate various kinds of anions. The positions of active sites are adjustable due to the use of selected metal cations and interlayer anions. LDHs are beneficial to harvesting visible light by controlling the metal cation. Furthermore, based on their anionic-exchange ability, LDHs are widely applied in wastewater treatment. Another important merit is the "memory effect" that can restore the original LDH structure and assist with exchanging the inorganic anions after the adsorption of various anions [76–80]. These special features of LDH materials allow them to exhibit a superior adsorption ability toward organic pollutants. Therefore, in light of these characteristics, the adjustable structure and constitution of LDHs make them potentially excellent photocatalytic materials [81]. Nevertheless, the removal capacity of pristine LDHs is immensely limited because of the low number of functional groups. LDH-based nanocomposites are synthesized via combining LDHs with other materials such as carbon nanomaterials, polymers, and surfactants. The nanocomposites possess improved surface area and better adsorption performance by harnessing the performance contributions of different materials compared to pure LDH [62,82,83]. Hence,

researchers have constantly been developing diversified modification strategies in order to make high-performance LDH nanocomposites for applications in multiple fields.

2.2 Synthesis of LDHs

The different synthetic method and design will impact the structure and chemical properties of LDHs. For example, Sahu *et al.* [84] successfully synthesized ZnAlTi LDHs by a simple co-precipitation method using varying Zn:Al:Ti atomic ratios as a precursor. The LDHs are prepared by blending metal cations with nanomaterials in alkaline solution. In detail, a mixed solution of $Zn(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, and $TiCl_4$ was added into stirred solution of Na_2CO_3, and retained the pH of solution at 10. Then, the resultant mixture was aged at room temperature for 18 h, collected by centrifugation, washed with distilled water and ethanol several times, and dried at 90°C in an air oven. Rahmanian *et al.* [85] reported that a novel adsorbent of Ni/Al-LDH was synthesized by a solvothermal method via the precipitation of metal nitrates. In a typical procedure, a salt solution containing $Al(NO_3)_3{\cdot}9H_2O$ and Ni $(NO_3)_2{\cdot}6H_2O$ was dispersed in the solution of Na_2CO_3 by ultrasonication for 30 min. Subsequently, NaOH solution (0.2 M) was added into the aforementioned mixture and stirred for 2 h to maintain the pH value of the solution at 10. Finally, the homogenous suspension was transferred into Teflon-lined stainless steel autoclaves and heated at 150°C for 8 h. Moreover, Abazari *et al.* [86] developed an NiTi-LDH through an optimized hydrothermal method. In their experiments, aqueous solution of metal salts (Ni $(NO_3)_2{\cdot}6H_2O$, titanium(IV) chloride, and NH_4F with the molar ratio of 2:1:3) was added in 50 mL of deionized water. Simultaneously, a solution of NaOH was dissolved to maintain the pH of the mixed solution at 5. The obtained mixture was stirred to ensure homogeneity of the reactants, then transferred to a Teflon-lined autoclave and heated for 48 h at 130°C. The final product was centrifuged and washed with ethanol and deionized water. The other methods such as anion-exchange, microwave, and calcination also are the frequently common and successful strategy to prepare LDH nanomaterials.

2.3 Mechanism of LDH as a photocatalysis

Photocatalyst is a potential material for environmental purification by utilizing solar energy to generate chemical energy. The electrons and holes are shifted to the surface of the photocatalytic materials under solar energy, which produce active species for redox reactions to remove pollutants [87–90]. Figure 2 obviously describes the mechanism of the photocatalyst [91]. While the ultraviolet (UV) light irradiation contacts with LDH photocatalyst, the electrons are activated to generate holes in the valence band. The charge was separated and transferred to the surface of the photocatalyst which produces hole charge carriers for the degradation of the pollution.

The photocatalytic performance of the LDHs is greatly hinge on the abundant active sites, specific surface area, and unique morphology. In addition, the narrow band gap of LDHs improved the activity of visible light absorption, making it effectively remove the contaminants in aqueous solution [92–94].

2.4 Construction of LDH-based ternary nanocomposites

2.4.1 Precipitation method

Precipitation process is the formation of a solid precipitation from a homogeneous solution in the presence of precipitating agent, which is also the most common approach for constructing LDH-based ternary nanocomposites. This method is employed widely for synthesizing composites on account of controllable reaction conditions, the effortless operation, and well-proportioned products [95–97].

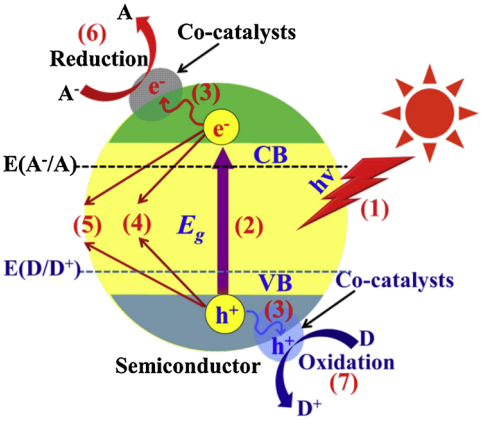

Figure 2: The fundamental mechanism of photocatalysis. Reproduced with permission from ref. [80]; copyright (2017), Elsevier.

For instance, a salt solution containing $Zn(NO_3)_2{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ was ultrasonically added into a suitable quantity of the prepared $NiFe_2O_4$ to obtain a uniform suspension [98]. Subsequently, a mixed solution of NaOH and Na_2EDTA was dispersed to maintain the pH at 10. The resulting mixture was aged for 8 h, followed by washing with ethyl alcohol and deionized water. Furthermore, Kandi *et al.* [99] reported $BiVO_4$/CdS/MgAl-LDH hybrid for the degradation of pollutant and water splitting under UV light irradiation. In their experiments, $BiVO_4$ was dispersed into mixed solution of $Cd(NO_3)_2{\cdot}2H_2O$ and thioglycolic acid (the molar ratio of 2:1). NaOH and Na_2S were added to the solution, which retained the pH at 10.5, and were stirred for 30 min at 65°C. The final product was washed with distilled water and dried in an oven for 24 h. Besides, Mureseanu *et al.* [56] synthesized g-C_3N_4/CuONP/LDH composite, which showed excellent photocatalytic ability for phenol reduction from aqueous solutions. Beyki *et al.* [100] developed MgAl@$CaFe_2O_4$–poly *o*-phenylenediamine nanohybrid for effective removal of lead(II), chromium(III), and anionic azo dye (Figure 3). Sahoo *et al.* [101] synthesized a Z-scheme dictated WO_{3-x}/Ag/ZnCr LDH for the degradation of tetracycline (TC) and H_2 evolution.

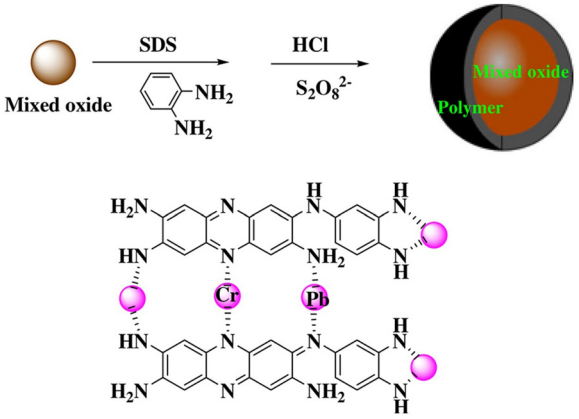

Figure 3: Schematic illustration of MgAl@$CaFe_2O_4$–poly *o*-phenylenediamine composite fabrication. Reproduced with permission from ref. [89]; copyright (2016), Elsevier.

2.4.2 Hydrothermal method

Hydrothermal method is the most simple and cost-effective technique to fabricate ternary nanocomposites that are of high purity. This method makes it easy to obtain well-crystallized product via adjusting the reaction conditions. The resulting LDH-based products can obtain an adequate reaction and good morphology in a hydrothermal system under high temperature and pressure [102–104].

For instance, a novel CoAl-LDH/g-C_3N_4/RGO ternary heterojunction was synthesized as follows: a certain amount of the obtained CN and GO powders was dissolved in 160 mL of aqueous solution and stirred for 10 min [105]. $Co(NO_3)_2{\cdot}6H_2O$ (0.006 M) and $Al(NO_3)_3{\cdot}9H_2O$ (0.002 M) were dispersed into the aforementioned suspension under constant ultrasonic agitation for 30 min. After that, urea (0.05 M) and NH_4F (0.016 M) were added to the aforementioned solution and stirred for 30 min. The hydrothermal reaction was carried out in a 200 mL Teflon-lined stainless-steel autoclave and heated at 120°C for 24 h. The final product was washed with deionized water several times and dried at 60°C. The schematic diagram for the synthesis of the ternary composites is shown in Figure 4. Bhuvaneswari *et al.* [106] constructed a r-GO/LDH/g-C_3N_4 nanocomposite to efficiently remove organic dry pollutants under visible light. In brief, a certain amount of g-C_3N_4 and r-GO was dispersed in 40 mL of deionized water, which was ultrasonicated for 15 min. A 0.5 M of $MgCl_2{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ were added to the aforementioned suspension. Subsequently, urea and NaOH were added into the mixed solution, then ultrasonicated for 15 min. Finally, the obtained suspension was moved to a 100 mL autoclave and heated at 180°C for 5 h in an oven. Furthermore, Bing *et al.* [107] reported that Bi_2O_3/Bi_2WO_6/MgAl-CLDH hybrids showed enhanced adsorption and catalytic performance toward Congo red and doxycycline degradation under solar light. In this process, the Bi_2O_3/Bi2WO_6/MgAl-CLDH composite was synthesized by using 2.4 mmol $Bi(NO_3)_3{\cdot}5H_2O$, 1 mmol $Na_2WO_4{\cdot}2H_2O$, and 0.3 g MgAl-LDH, which were suspended in 20 mL of ethylene glycol via ultrasonic treatment for 10 min. After that, the mixture was transferred into a stainless-steel autoclave and heated at 160°C for 6 h. The final product was obtained and washed with deionized water.

2.4.3 Solvothermal method

The solvothermal technique is based on the hydrothermal method, and the synthesis condition use organic solvents as reaction media instead of water. This approach can facilitate the stability of the products and the dispersity of precursors by using organic solvent during chemical reactions [108,109]. The low-boiling point of organic solvents is beneficial to product crystallization under high pressure. Hence, solvothermal method was widely employed for constructing LDH-based ternary nanocomposites in

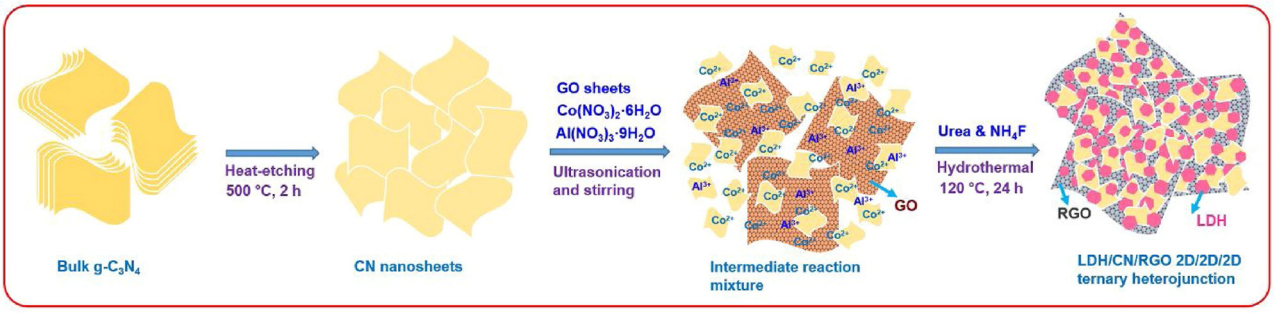

Figure 4: Preparation of the CoAl-LDH/g-C_3N_4/RGO ternary photocatalyst. Reproduced with permission from ref. [94]; copyright (2019), Elsevier.

many research. Liu *et al.* [110] synthesized a novel TiO_2/BiOCl/ZnCr-LDH composite for visible-light photocatalytic degradation of Rhodamine B via a facile solvothermal process. In this synthesis process, a certain amount of tetrabutyl titanate was treated with 50 mL of ethanol to form the suspension by mechanical agitation. A 0.2 g of BiOCl/ZnCr-LDH was dissolved into the aforementioned solution through ultrasonic treatment for 30 min. The resulting product was obtained from a 50 mL Teflon-sealed autoclave at a temperature of 150°C for 20 h. The study demonstrates that this strategy is simple, effective, and economical for the synthesis of nano-catalysis materials.

3 Application of pollutant removal

3.1 Organic dyes

In recent years, the pollution of organic dyes has received wide attention with the rapid development of industrialization. However, it is difficult to remove with traditional techniques due to high stability of many organic dyes in aqueous solution [111,112]. The photocatalytic technique is extensively investigated to apply for the degradation of organic dyes [113–115]. Particularly, LDH-based ternary composites can greatly improve the photocatalytic activity, which are widely used for environmental applications. Herein, the application and performance of LDH-based ternary nanocomposites are discussed and reviewed.

Zhou *et al.* [116] prepared Pd(II)/Bi_2O_3/MgAl-LDH by the impregnation technique and calcined reconstruction, which revealed excellent photocatalytic ability for decomposition of MB under visible-light irradiation. The BET surface area of Pd(II)/Bi_2O_3/MgAl-LDH ternary composites is 48.4 $m^2 g^{-1}$, which is analyzed by a BET instrument. The photocatalysis of high crystallinity and hierarchical structure was observed from scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images. Besides, the result of UV-vis diffuse reflectance spectroscopy (DRS) showed that Pd(II)/Bi_2O_3/LDH possess a broad absorption in the visible light region because of a low band gap of 2.19 eV. The chemical composition of the samples was detected by energy dispersive X-ray analysis and inductively coupled plasma-atomic emission spectrometry. Figure 4(d) indicates that Pd was doped in Bi_2O_3/LDH. Cycling experiments of Pd(II)/Bi_2O_3/LDH photocatalyst were executed to measure the stability. After four successive cycles, the photocatalytic activity still remains stable, indicating its enormous potential application as photocatalysis.

The construction of a novel $BiVO_4$/CdS/MgAl-LDH with visible light-driven photocatalysis was achieved and applied to degrade methyl orange (MO) and TC [99]. The $BiVO_4$/CdS/MgAl-LDH photocatalyst degrades 92 and 51% of TC and MO in 60 min, respectively. The UV-vis DRS is used to evaluate the optical absorption value of composites. The Z-scheme photocatalysts generated a good deal of O_2 and H_2 under UV light irradiation. The result of experiment demonstrated that the synergistic effect of $BiVO_4$, CdS, and LDH can effectively enhance the photocatalytic performance.

Bing *et al.* [107] employed efficient hydrothermal method for the fabrication of heterojunction Bi_2O_3/Bi_2WO_6/MgAl-CLDH nanocomposite (Figure 5). SEM, TEM, and high-resolution transmission electron microscopy (HRTEM) analyses were employed to investigate the microstructure and morphology of Bi_2O_3/Bi_2WO_6/MgAl-CLDH. It is found that the synthesized nanocomposites were made up of MgAl-LDH, Bi_2WO_6, and Bi_2O_3, which strongly proves the formation of heterojunctions. Compared with pure Bi_2O_3 and Bi_2WO_6, the PL intensity of Bi_2O_3/Bi_2WO_6/MgAl-CLDH displayed the weakest peaks, indicating that the recombination rate of electron–hole pairs is the slowest. The ternary heterojunction exhibited enhanced photocatalytic

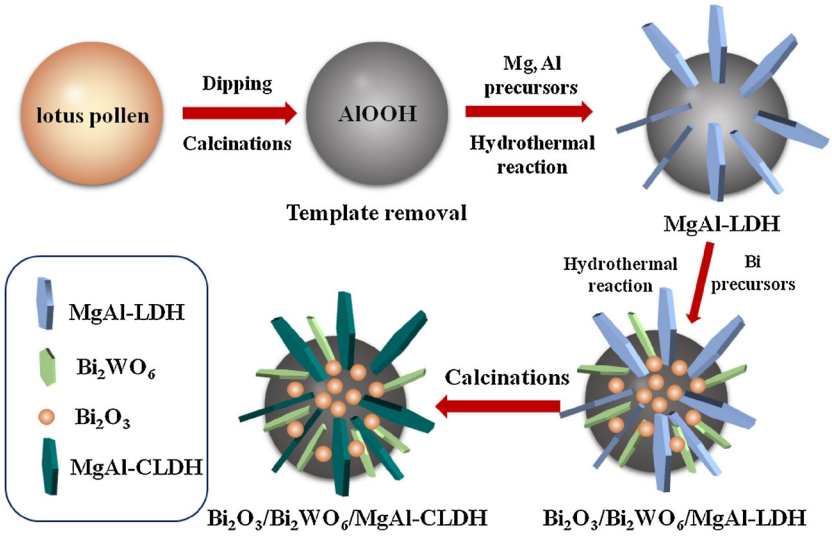

Figure 5: The synthesis process of Bi_2O_3/Bi_2WO_6/MgAl-CLDH. Reproduced with permission from ref. [96]; copyright (2018), Elsevier.

activity on account of the high separation efficiencies of charge carriers, hierarchically porous structure, and synergic interaction of adsorption and photocatalysis. A total of 71.43% Congo red and 82.85% doxycycline were removed within 60 min under sunlight irradiation, respectively.

More recently, Tonda and Jo [117] studied a novel Ag/LDH/g-C_3N_4 nanocomposite with Ag nanoparticles decorated NiAl-LDH/graphitic carbon nitride that enhanced the photocatalytic performance for the degradation of aqueous Rhodamine B and 4-chlorophenol. The SEM, TEM, and HRTEM images showed that spherical Ag NPs are uniformly distributed on the surface of LDH/CN and the size of the Ag NPs was in the range of 10–20 nm (Figure 6). Combining with the data of XPS measurements, it is observed that Ag/LDH/g-C_3N_4 is composed of Ag, LDH, and CN. UV-vis DRS curves of all the photocatalysts display that Ag/LDH/CN nanocomposites have broader light absorption than pure LDH and CN. The improved photocatalytic activity was likely ascribed to rapid charge transfer, surface plasmon resonance, and unique structure. The high structural stability of Ag/LDH/g-C_3N_4 nanocomposites ensured no significant change in degradation activity after successive experimental runs.

Jo *et al.* [118] reported that a Cu/TiO_2/LDH photocatalyst exhibited remarkable performance for the degradation of MO under visible light irradiation (Figure 7). The analysis result of UV-vis diffuse reflectance spectral displayed that visible-light absorption is further extended by doping Cu on TiO_2/LDH composites. The morphology observation and microstructure of Cu/TiO_2/LDH composites showed that the TiO_2 nanoparticles were uniformly decorated on the flower-like LDH microspheres by SEM

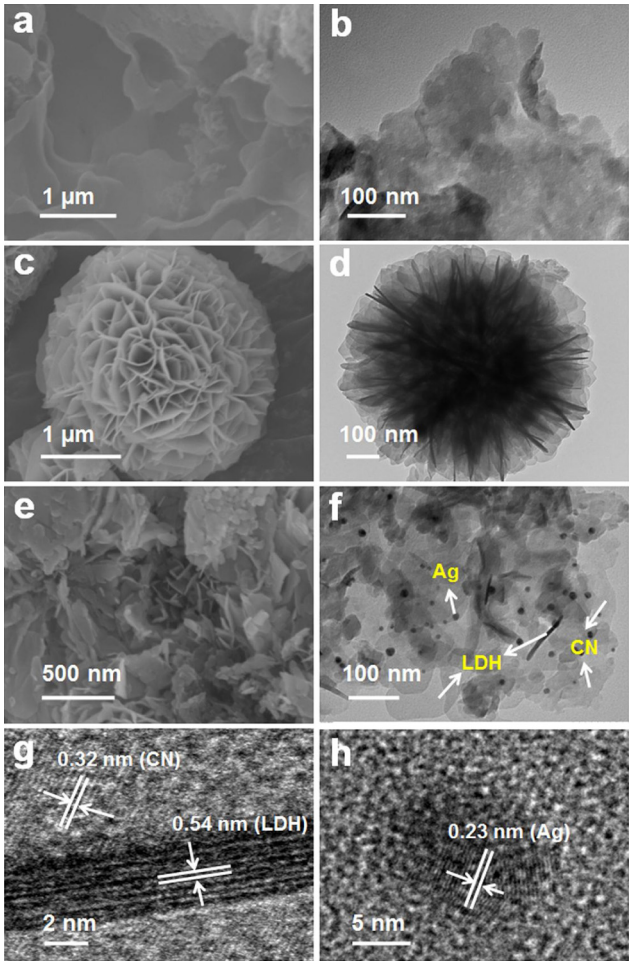

Figure 6: (a, c, and e) SEM and (b, d, and f) TEM images of CN, LDH, and the ALDHCN-15 samples, respectively. (g and h) High-resolution TEM images of the ALDHCN-15 nanocomposite. Reproduced with permission from ref. [106]; copyright (2018), Elsevier.

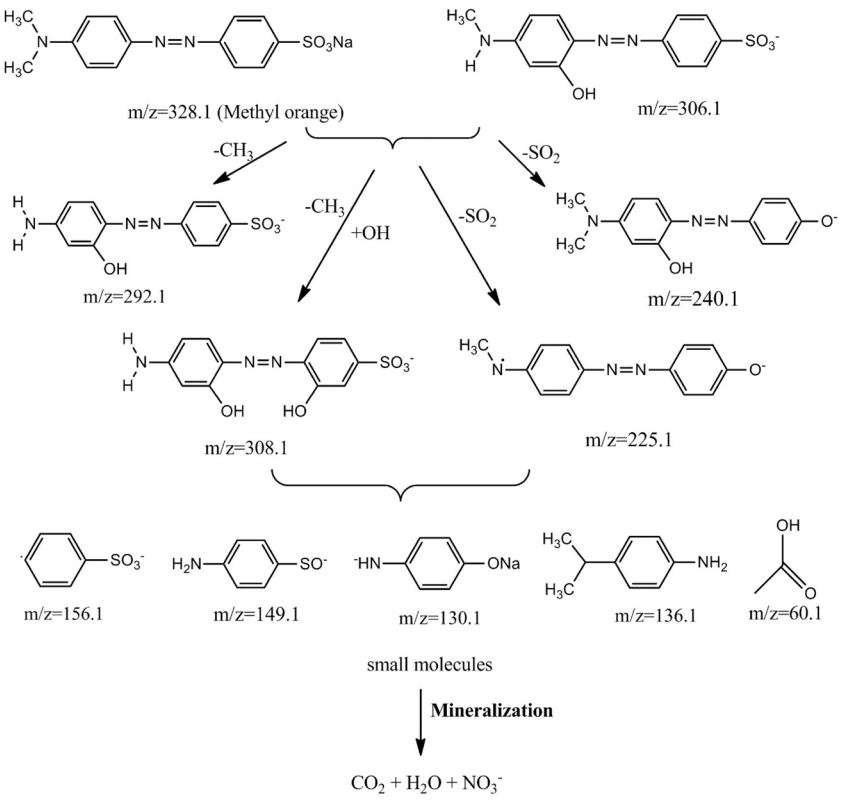

Figure 7: Proposed degradation pathway of MO under visible-light illumination using Cu/TiO_2/LDH-30 catalyst. Reproduced with permission from ref. [107]; copyright (2018), Elsevier.

and TEM analyses. In addition, the pore diameter and BET surface area of the composite were higher than those of the single LDH and TiO_2 samples. The Cu/TiO_2/LDH composite (30 wt% of Cu/TiO_2 on P-CN) displayed the optimal photocatalytic activity and highest stability among the synthesized photocatalysts.

Li *et al.* [119] successfully synthesized a novel Ag@TiON/CoAl-LDH photocatalyst with catalytic memory activity through a dark deposition method. The absorption edge of composite material was shifted into the visible light area via the introduction of Ag nanoparticles and LDH nanosheet, which effectively improved the efficiency of light absorption and charge separation. The Ag@TiON/CoAl-LDH nanocomposite showed higher photocatalytic ability than pure TiON and CoAl-LDH for the degradation of MO and the removal efficiency reaches 94%. A possible mechanism for the photocatalytic reaction is shown in Figure 8.

In a research, Liu *et al.* [110] reported that a novel TiO_2/BiOCl/ZnCr-LDH composite was synthesized via a facile solvothermal method for photocatalytic decolorization of Rhodamine B. The SEM and TEM images of the TiO_2/BiOCl/ZnCr-LDH heterostructure showed that the BiOCl nanosheets and TiO_2 nanoparticles were deposited sequentially on the surfaces of ZnCr-LDH material (Figure 9). The co-catalyst can generate synergistic effect to enhance the photocatalytic properties by depositing BiOCl and TiO_2 on the surface of ZnCr-LDH. Furthermore, the stability of composite materials is still maintained at a high level for at least three cycles.

Jo *et al.* [105] evaluated a novel LDH/CN/RGO ternary heterojunction photocatalysis with a 2D/2D/2D configuration for elimination of aqueous Congo red under visible light irradiation. UV-vis DRS studies revealed that LDH/CN/RGO conducts a clear red shift compared with binary materials, which possess a significant light absorption capacity. TEM and HRTEM images show that several LDH nanoflakes are freely distributed on the surface of CN and RGO (Figure 10a and b). The results of elemental mappings further verified the intimate interfacial contact of CN, LDH, and RGO (Figure 10c–h). The LDH/CN/RGO ternary heterojunctions exhibited enhanced photocatalytic property and good stability through the large intimate interfacial contact among constituent CN, LDH, and RGO, which effectively prevents the recombination of the photoinduced electron–hole pairs.

Recently, Bhuvaneswari *et al.* [106] reported that a reduced graphene oxide supported g-C_3N_4/NiMgAl-LDH

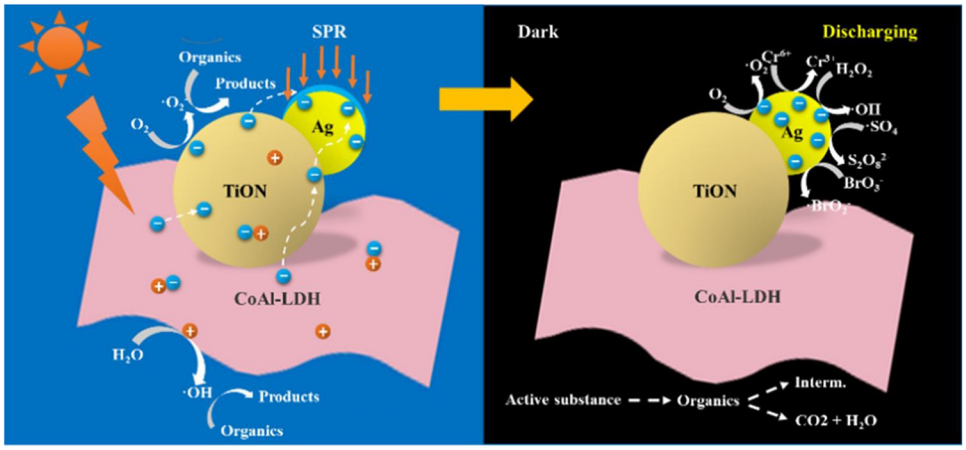

Figure 8: Mechanism of the photocatalytic reaction. Reproduced with permission from ref. [108]; copyright (2020), Elsevier.

composite system was synthesized by using the hydrothermal process. The degradation efficiency of the r-GO/g-C_3N_4/LDH hybrid was evaluated under visible-light irradiation, and it shows excellent photocatalytic activity and good reusability. The introduction of r-GO and g-C_3N_4 improves the charge carrier separation efficiency, which remarkably enhanced the degradation performance of organic dye. The enhanced photocatalytic activity is

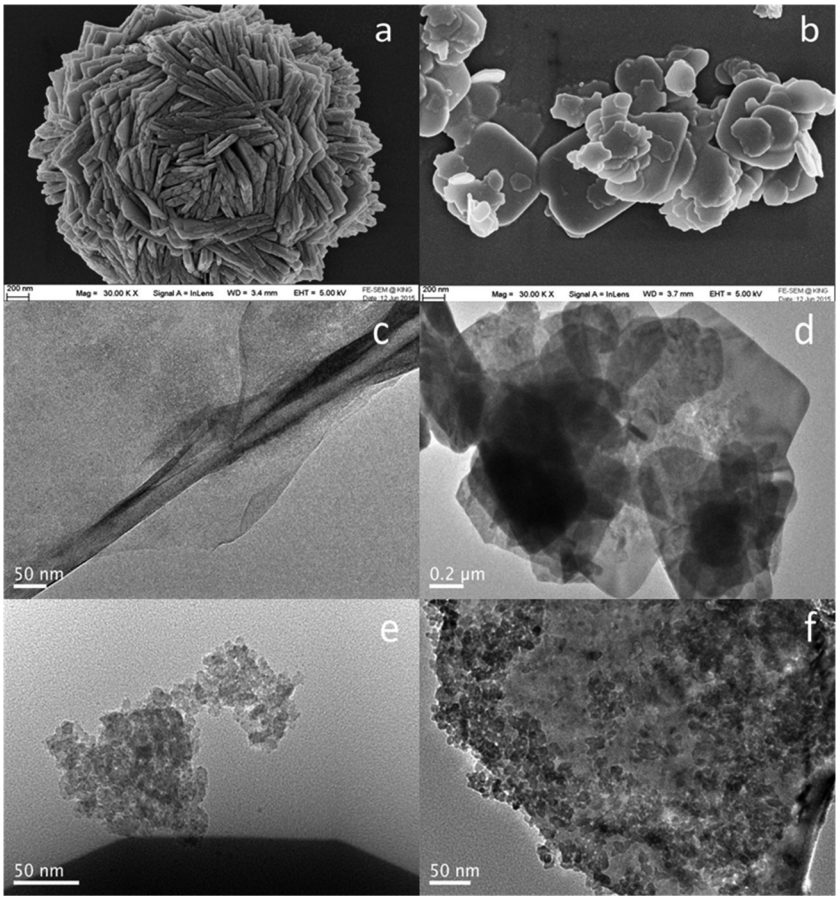

Figure 9: SEM images of (a) pure BiOCl and (b) BiOCl-ZnCr-Ex and TEM images of (c) ZnCr-Ex, (d) BiOCl-ZnCr-Ex, (e) pure TiO_2, and (f) TiO_2-BiOCl-ZnCr-Ex-4. Reproduced with permission from ref. [99]; copyright (2017), Elsevier.

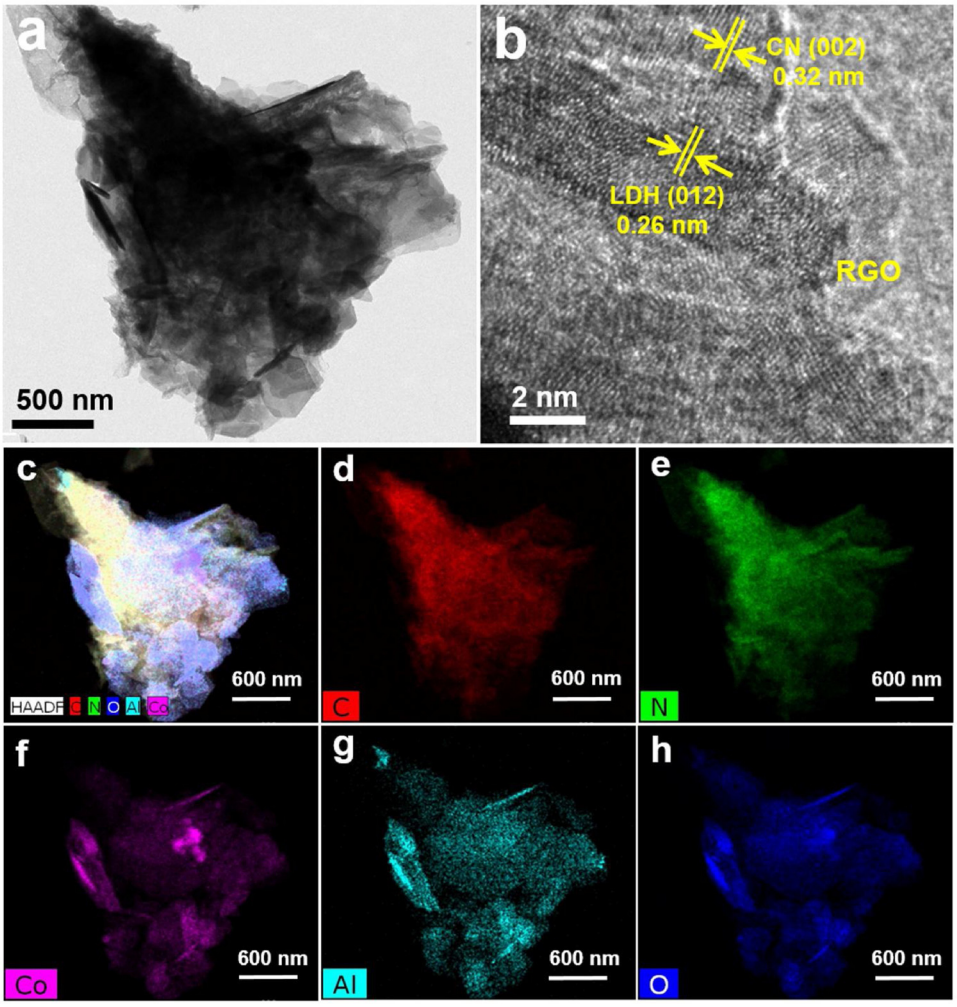

Figure 10: TEM (a) and HRTEM (b) images of the LCR-15 photocatalyst. EDS elemental mappings of constituent elements in the LCR-15 photocatalyst (c–h). Reproduced with permission from ref. [94]; copyright (2019), Elsevier.

likely attributed to the synergistic effect of rapid charge transfer and inhibition of electron–hole recombination. Figure 11 exhibits the photocatalytic reaction mechanism of MB dye degradation.

3.2 Heavy metal ions

The pollution of heavy metals from industrial discharge has resulted in a serious threat to human health and life on account of high toxicity and degradation resistance, which has widely aroused the public concern [120]. Various approaches have been developed for eliminating heavy metals from wastewater. Among various methods, considerable attention has been paid to the photocatalytic reduction method because of excellent properties such as high efficiency and no secondary pollution. Herein, some literature about the LDH-based ternary composites for the removal of metal ions is summarized.

Nayak and Parida [55] reported that a new heterostructure Ag@Ag_3PO_4/g-C_3N_4/NiFe-LDH photocatalyst was synthesized through an electrostatic self-assembly and in situ photoreduction method (Figure 12). The combination of Ag_3PO_4 as a p-type semiconductor and the surface plasmon resonance effect of metallic Ag NPs on g-C_3N_4/NiFeLDH could greatly enhance the photocatalytic efficiency for Cr(VI) reduction under visible light. The morphology and microstructure of the resulting compound are observed by TEM and HRTEM analyses, which revealed a unique spherical Ag NP and Ag_3PO_4 inset into the g-C_3N_4/NiFe-LDH hybrid materials. The surface chemical composition of the nanocomposites is analyzed by the X-ray photoelectron spectroscopy (XPS), further confirming the formation of ternary heterostructures. The photocatalytic

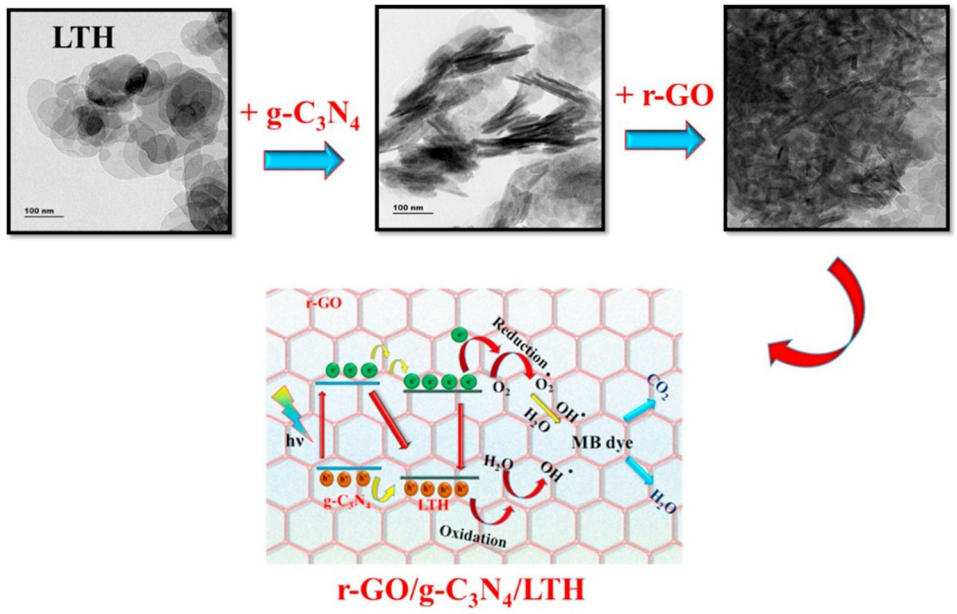

Figure 11: Schematic image of possible photocatalytic reaction mechanism of MB dye degradation. Reproduced with permission from ref. [95]; copyright (2020), Elsevier.

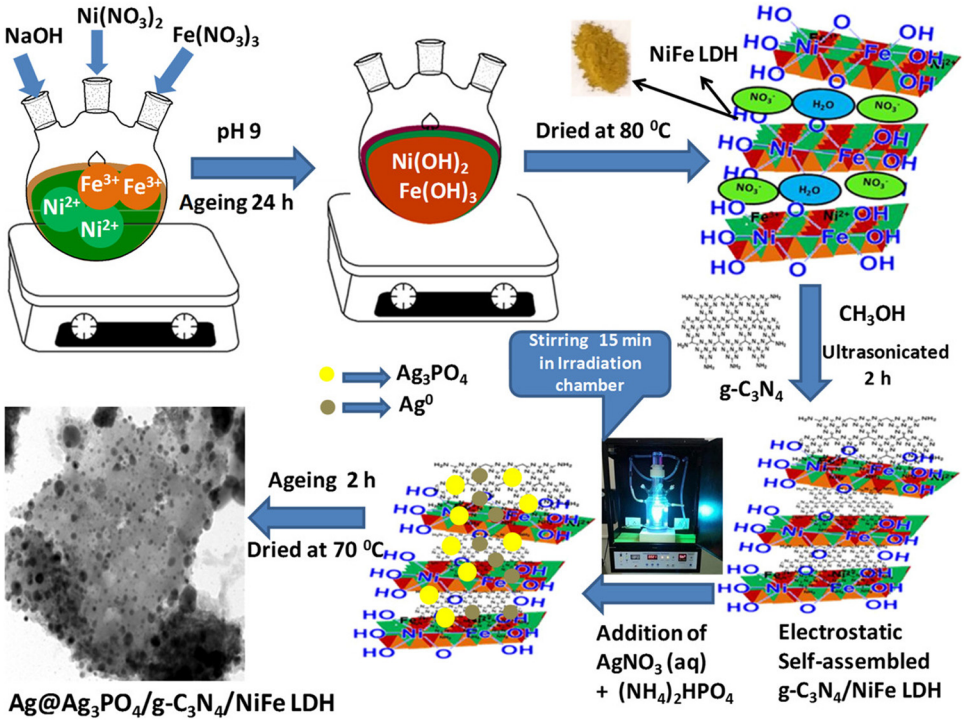

Figure 12: Synthetic steps of the heterostructure $Ag@Ag_3PO_4/g\text{-}C_3N_4$/NiFe-LDH nanocomposite. Reproduced with permission from ref. [45]; copyright (2018), American Chemical Society.

activity of $Ag@Ag_3PO_4/g\text{-}C_3N_4$/NiFe-LDH heterojunction showed a photocatalytic Cr(VI) reduction rate of 97% for 2 h.

Das *et al.* [121] successfully developed a novel magnetically separable Au-loaded $CaFe_2O_4$/CoAl-LDH heterostructure through sol–gel and borohydrate reduction method. The TEM image of the Au/$CaFe_2O_4$/CoAl-LDH heterostructure confirmed that the Au nanoparticles are attached into $CaFe_2O_4$/CoAlLDH heterostructures. The results of inverted V-shaped M–S plot revealed the existence of an innermost contact interface between $CaFe_2O_4$

and CoAl-LDH, which improves the efficiency of separation and transfer of charge pairs. The Au@CoAl-LDH/$CaFe_2O_4$ ternary heterostructure exhibited an excellent Cr(VI) removal rate under visible light irradiation and high stability during repetitive experiment. The superior photocatalytic performance of the obtained nanocomposites was attributable to the surface plasmon effect and formation of a p–n junction by increasing the contact area.

3.3 Antibiotics and pesticides

Environmental pollution, especially pesticide and antibiotics, has attracted much attention owing to an enormous threat to human health, which is one of the most urgent ecological problems to be solved [122–125]. Therefore, it is imperative to remove pesticides and antibiotics in the aqueous solution.

Sahoo *et al.* [101] reported that a novel Z-scheme WO_{3-x}/Ag/ZnCr-LDH photocatalyst was prepared through coupling with Ag nanoparticle, nonstoichiometric WO_3, and ZnCr-LDH nanosheet. The photocatalytic efficiency of the resulting compound was estimated under visible light irradiation. The results of BET show that WO_{3-x}/Ag/ZnCr-LDH ternary nanomaterials possess larger specific surface area than the pure LDH and WO_{3-x} materials, which can provide abundant reaction sites for improved photocatalytic performance. The WO_{3-x}/Ag/ZnCr-LDH ternary heterostructure displayed excellent performance of TC degradation, which was attributed to the rapid separation efficiency of charge carriers through the Z-scheme system. Furthermore, the oxygen deficiency of WO_{3-x} further enhanced the catalytic ability of composites by restraining the recombination of photoexcited electron–hole pairs.

Ni *et al.* [42] successfully developed a NiAl-LDH/Fe_3O_4/RGO composite for the degradation of ciprofloxacin (CIP) under visible light irradiation. The results of SEM and TEM revealed that NiAl-LDH nanosheet and Fe_3O_4 nanoparticles sized around 15 nm were uniformly distributed on the surface of RGO sheets. The XPS spectra of the as-prepared nanocomposites were used to analyze the surface chemical and valence states, which further demonstrated the formation of heterojunction. Besides, it was found that the degradation effectiveness of the NiAl-LDH/Fe_3O_4/RGO was 1.5 and 3 times more than that of NiAl-LDH/RGO and NiAl-LDH, respectively. The addition of RGO and Fe_3O_4 greatly improves the migration rate of charge carriers and the absorption of visible light for the degradation of CIP from aqueous solution. Meanwhile, the NiAl-LDH/Fe_3O_4/RGO photocatalyst provided more active species, which played critical roles in the degradation of CIP.

Fe_3O_4/Cs_xWO_3/NiAl-LDH composites were fabricated through a hydrothermal method for the degradation of 2,4-dichlorophenoxyacetic acid, which can almost completely remove 2,4-dichlorophenoxyacetic acid in 180 min. In addition, the high reusability and stability of the photocatalysts can still be maintained after four circulation runs [126]. The mechanism of improved peroxymonosulfate (PMS) activation with Fe_3O_4–Cs_xWO_3/NiAl-LDH heterojunction is demonstrated in Figure 13.

The aforementioned illustration summarized applications of LDH-based ternary nanocomposite as a photocatalyst for the removal of contaminants in water. In this review, the photocatalyst systems of LDH-based ternary will provide basic insights and helpful instruction for the diversified applications.

4 Conclusion and perspectives

In this review, recent development on the manufacture and applications of LDH-based ternary photocatalyst for the degradation of organic dyes, heavy metal ion, antibiotics, and pesticides has been summarized. Different preparation approaches such as simple precipitation method, hydrothermal method, and solvothermal method have been applied to construct the LDH-based ternary heterojunction. The formation of LDH-based ternary composite significantly enhanced photocatalytic performance, which is ascribed to large specific surface area, wide

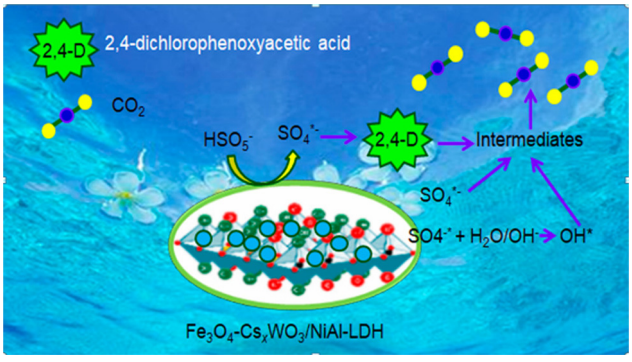

Figure 13: Schematic diagram of the photocatalytic process occurring on the surface of Fe_3O_4–Cs_xWO_3/NiAl-LDH composites. Reproduced with permission from ref. [115]; copyright (2018), American Chemical Society.

spectral response, abundant reaction sites, excellent electron conductivity, and inhibition of electron–hole recombination. To date, despite significant improvement in LDH-based ternary photocatalyst, there are many matters and challenges to be explained for further optimizing the property of material and photocatalytic reaction mechanism. Therefore, the following points may be taken into consideration:

1. At present, LDH-based ternary composites mainly aim at photocatalytic degradation of organic pollutant and heavy metal in aqueous solution. The researchers should focus on the application for photocatalytic water splitting, CO_2 reduction, and nitrogen fixation.
2. Explore the reaction mechanism of reactants and the LDH-based ternary photocatalysts. The reaction conditions should be further optimized in different applications.
3. LDH-based ternary hybrids are only researched for the removal of single pollutant. Hence, testing the performance of nanocomposite in multi-pollutant system is recommended.
4. The hazard assessment and cost effectiveness of LDH-based ternary photocatalysts should be considered in the synthesis of nanomaterials.

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