

Nanostructured layered double hydroxides based photocatalysts: Insight on synthesis methods, application in water decontamination/splitting and antibacterial activity

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Abstract

Recently, layered double hydroxides (LDHs) materials have attracted increasing attention in various environmental applications. They offer the advantages of relatively simple synthesis methods, low fabrication cost, possession of reasonable specific surface area, high catalytic activity, great anion exchange capacity and good thermal stability. Therefore, these materials have been tested in a wide range of applications such as absorbents, catalysts, additives for polymer composites, sensors and supercapacitors. Several researches have been devoted to develop the preparation routes of LDHs in order to improve the potentiality of these solids to decontaminate water by photocatalytic process, and enhance their photocatalytic performances for energy storage applications specifically water splitting. This study provides an overview of the researches from recent studies done on different common synthesis methods of LDHs, including the co-precipitation, ion-exchange, reconstruction, hydrothermal and sol-gel methods. A few approaches have been investigated for LDHs modification such as polyol method, exfoliation/restacking, solvothermal and microwave techniques. In addition, this study aims to give insight on the recent applications of LDHs in heterogeneous photocatalysis process for the degradation of organic pollutants, water splitting for H₂ and O₂ production and discuss the ability of LDH in the pathogen's inactivation.

Keywords: Layered double hydroxides (LDHs); Photocatalytic degradation; Water splitting; Antibacterial activity.

1. Introduction

Layered double hydroxides (LDHs) have received a lot of attention in various chemistry fields last years due to their potential properties including low-cost, facile preparation, high surface area, different chemical composition and ability to capture organic and inorganic anions [1][2][3]. These synthetic materials are a group of inorganic two dimensional (2D) nanostructured materials of basic nature and termed as class of anionic clays which adopt hydrotalcite like structure [4][5]. The important features of these materials enable them to be applied as potential candidates in many applications such as adsorbents for anionic molecules owing to the great ability to anion exchange between the anion intercalated in the basal spacing and the target anion to be removed. Calcined LDHs have also a high capacity to remove anionic dyes due to their reconstruction effect and rehydration upon dispersion in anionic solution (memory effect) to recover back to the lamellar structure. LDHs solids are also known as precursors of metal oxide photocatalysts and have been the subject of research in many publications because of their excellent properties like large surface area, thermal stability and the production of more reactive species on the surface of the photocatalyst under irradiation. In the same spirit, the LDHs have another application in the biomedicine fields, they can be deployed as potential drug delivery owing to their chemical stability, biocompatibility and the great pH dependence of the solubility of poorly soluble drugs [6].

The general formula of a LDHs is: $[M^{II}_{1-x}M^{III}_x(OH)_2]^x \cdot (A^{n-})_{x/n} \cdot mH_2O$, where M^{II} represents a divalent cation (Mg^{2+} , Zn^{2+} , Mn^{2+} , Ni^{2+} , Fe^{2+} ...), M^{III} represents a trivalent cation (Fe^{3+} , Co^{3+} , Al^{3+} , Cr^{3+} , Mn^{3+} ...), A^{n-} the compensating anion (NO_3^- , Cl^- , ClO_4^{2-} , CO_3^{2-} ...), where n is the charge of the anion, and m is the amount of interlayer water molecules. The coefficient x is equal to the $M^{III}/(M^{II}+M^{III})$ molar fraction and generally ranges from [0.17 to 0.33] [7]; if this value exceeds this range, the formation of pure hydroxides is observed with the presence of impurities and other compounds [8]. The elemental composition and molar fraction directly influence the morphology, crystal structure and the basal spacing of LDHs and therefore impact on their applications [9][10]. The thermal decomposition of LDHs materials allows to produce mixed metal oxides, which have hexagonal or spinel-like phases exhibiting synergetic effects between the elements depending on the chemical composition, synthesis method, molar ratios and calcination temperature [10]. In the same vein, the development of LDHs at the laboratory scale leads the researchers to increase their efforts to modify and develop methods for synthesizing these materials in order to produce appropriate LDHs structure with more sophisticated and advanced characteristics that subsequently allow them to be employed in a wide range of fields.

The crystallinity, morphological and physico-chemical properties of LDHs structure depend significantly on the composition, activation process and synthesis method notably co-precipitation, ionic exchange, reconstruction, sol-gel, hydrothermal, etc. Each of these methods has own advantages and drawbacks and at the same time gives rise to materials with different morphologies and semiconductor properties, which in turn requires careful selection of suitable synthesis methods of LDHs before being applied in the target application.

LDHs obtained through co-precipitation method showed high purity and crystallinity. This approach is described by simultaneous precipitation of metal salts $M(OH)_2$ and $M(OH)_3$ and alkaline solution at constant pH. It allows the formation of hydroxide structure intercalated with nitrates or carbonates in their interlamellar domains because of high affinity of carbonates to the basal spacing. The formation of layered double hydroxide by co-precipitation could be described by nucleation and growth/aging procedure [11][12]. However, it involves some drawbacks such as aggregation, which occurs by the presence of a small amount of an amorphous phase [13]. The aggregation of the LDHs particles prevents accessibility to the most active sites that have a low coordination at the materials surface. The hydrothermal synthesis process in a Teflon-lined stainless steel jacketed reactor is another method similar to the co-precipitation technique, which the particles size and morphology could be controlled [14]. This method allows to obtain LDHs materials with high crystallinity [15]. The intercalation of some anions in the lamellar domains of LDHs not adapt to conventional process, therefore, the ions exchange or reconstruction methods are considerably suitable process to obtain LDHs materials intercalated with targets anions [16][17]. Using organic solvents and other synthesis methods such as sol-gel, polyol medium, solvothermal considered as solution promising overcome problems resulting through conventional synthesis methods like co-precipitation, hydrothermal and ions exchangers, which not beneficial for some metal salts precursors that are not soluble in aqueous solution.

In other respect, the metal oxides semiconductors derived from LDHs are considered as alternative photocatalysts for water purification, due to their great specific surface area and their ability to produce reactive species under irradiation. These kind of materials have been considerably studied in several fields of photocatalytic degradation of organic pollutants [10], since environmental pollution has appeared as an important issue [18][19][20][21]. Moreover, the great potential of LDHs based photocatalysts allows the renewable energy conversion through water oxidation electrocatalysis making it as the most efficient process for H_2 generation and O_2 evolution [22][23][24]. LDHs -derived photocatalysts have an ability to generate active species, they can be used as antibacterial agents against many pathogenic

bacteria [25], which also shows that these materials could be effectively applied in the biological area [26].

This review highlights a global summary which aims to reveal the latest evaluation of the development of synthesis methods of LDHs with current various approaches. Subsequently, various applications such as photocatalytic degradation of organic pollutants, antibacterial tests and water splitting for H₂ and O₂ production has been also discussed.

2. Synthesis routes of LDHs

Layered double hydroxides (LDHs), known as ionic lamellar compounds, are generally simple to synthesize in the laboratory. There are different routes designed for the preparation of LDHs and each method has its own unique advantages and disadvantages when compared to other methods.

2.1. Common methods for the synthesis of LDHs

2.1.1. Co-precipitation

The frequently common used technique for LDHs preparation is co-precipitation [10][27][28][29][30][31][32]. This method involves the mixing of aqueous solutions of the divalent and trivalent cations, containing the anions that are to be intercalated into the LDHs (Fig.1). For simultaneous precipitation of two or more cations, the synthesis is carried out under supersaturation conditions. Co-precipitation at low supersaturation requires the slow addition of mixed solutions of divalent and trivalent metal salts with appropriate ratio into a reactor which contains an aqueous solution of the desired interlayer anion. In order to promote co-precipitation of both the metal salts, a second solution of an alkali is introduced simultaneously while keeping the pH fixed. In contrast to the first method, coprecipitation at high supersaturation is performed by drop-wise addition of a solution containing mixed metal salts to an alkaline solution containing the desired interlayer anion. In general, coprecipitation at high supersaturation gives rise to less crystalline materials due to the formation of a large number of crystallization nuclei. This method requires prolonged washing to reduce the amount of residual alkali because of the low solubility of the alkali bicarbonates. After precipitation, a thermal treatment process is carried out in order to increase the purity and crystallinity of the materials. This step is followed by an ageing process performed for a period ranging from a few hours to some days. Ivanova et al. [33] have investigated the synthesis of (Mg/Al) Layered double hydroxides by two co-precipitation methods at low and high supersaturation for nitrate removal. The both processes lead to the formation of similar crystalline compounds correspond to the layered structure of hydrotalcite-like materials thanks to the continuous regulation of the pH and long synthesis duration time (18 hours). In another similar study, Nguyen Tran et al.

[34] produced a typical hexagonal platelet-like morphology Mg-Al (LDHs) with particles dimension ranging from 100 nm to 300 nm. Berner et al. [35] used co-precipitation method for the preparation of Cu/Al and Cu/Cr layered double hydroxide (LDHs). The results demonstrated that Cu-Al LDHs exhibited a highest crystallinity than Cu-Al/Co LDHs and a particles size around 150 nm. Despite the difference between the crystallinity of both samples, the morphologies of these particles were similar and the specific surface area values around 50 m²/g for both Cu-Al LDHs and Cu-Al/Co LDHs. However, this process was not able to synthesis well-ordered Cu-Cr LDHs, which leads to a poor crystallinity and more amorphous structures of the materials obtained, while Cu-Cr LDHs and Cu-Cr/Co LDHs achieved a highest specific surface area compared to Cu-Al LDHs and Cu-Al/Co LDHs.

The crystallinity and the morphology of materials synthesized were affected by high supersaturation coprecipitation method [36], and demonstrate large dimension of the obtained particles due to the effect of hydrothermal treatment. However, due to the larger aggregate size, the specific surface area values of the samples prepared by coprecipitation at high supersaturation (between 50 and 100 m²/g) are lower than those obtained by sol–gel method (150–200 m²/g) [37][38]. Hydrothermal treatment or microwave irradiation, can effectively improve the crystallinity and the morphology of the materials. Othman et al. [39] studied the effects of thermal treatment on the micro-structures of co-precipitated and sol–gel synthesized Mg-Al LDHs. The results showed that the LDHs obtained from Sol-gel process exhibited specific surface area and pore sizes significantly increased.

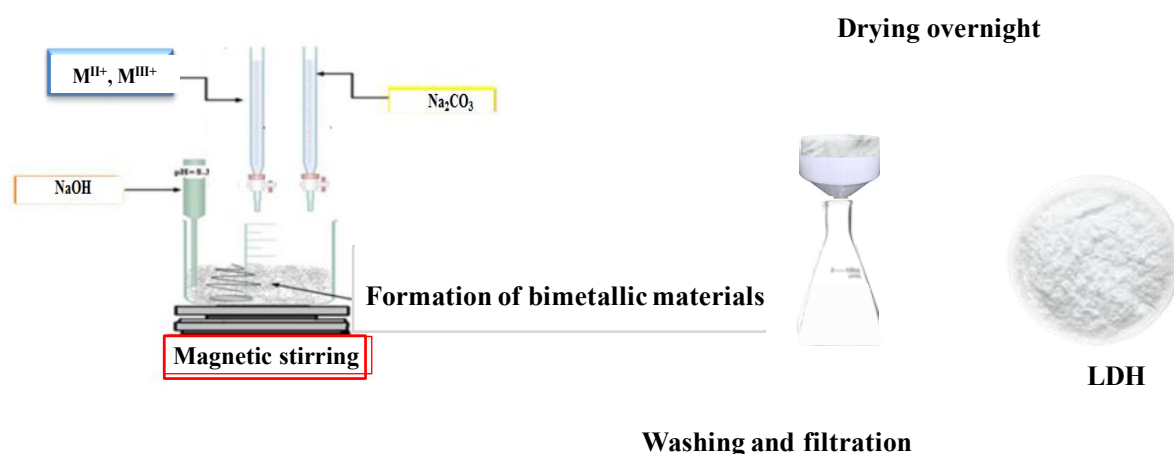


Fig.1. Schematic illustration of co-precipitation techniques applied to LDH synthesis.

2.1.2. Ion exchange

Ion exchange is another common method used to synthesis LDHs. This method is useful for the intercalation of a number of different types of anions between positively charged LDHs laminations [31][40][41][42][43]. It involves the exchange of host anions (CO_3^{2-} , NO_3^- and Cl^-)

or the guest anions with the anions present in the interlayer regions of LDHs, by stirring the pristine LDHs in a solution containing an excess of target anions (Fig. 2). The ion exchange process generally depends on the electrostatic forces between the LDHs lamellar layers and the exchangeable anions. It is effectively used when the coprecipitation process is inapplicable. While, some divalent or trivalent metal cations or the suitable anions are unstable in the alkaline solution, or the metal cations and the anions involved are directly more reactive, the ion-exchange can be considered as attractive method to produce the suitable LDHs [30]. In this method the target anions are successfully exchanged with the anions present in the interlayer regions of LDHs in favorite conditions to obtain specific anion-pillared LDHs. Zou et al. [44] has reported the anion exchange process as an effective method for the conversion of Ni-Co-CO₃ layered double hydroxide (LDHs) nanosheet arrays in an alkaline solution to Ni-Co-OH LDHs to improve the superior performance of the LDHs electrode of a reservoir for OH⁻ anions and obtain a better rate capacity, excellent coulombic efficiency, and great cycling stability. Another study [45] demonstrated that this method is not valid for exchanging all the anions such as carboxylates in the spacing basal of hydrotalcite structure, the exchange of the interlayer anions was not significantly affected by the direct exposure of LDHs materials to aqueous solution of guests anionic species because of the carbonate anion being more tenaciously held in the LDHs interlamellar region. The following order of exchange for mono and divalent anions has been derived:

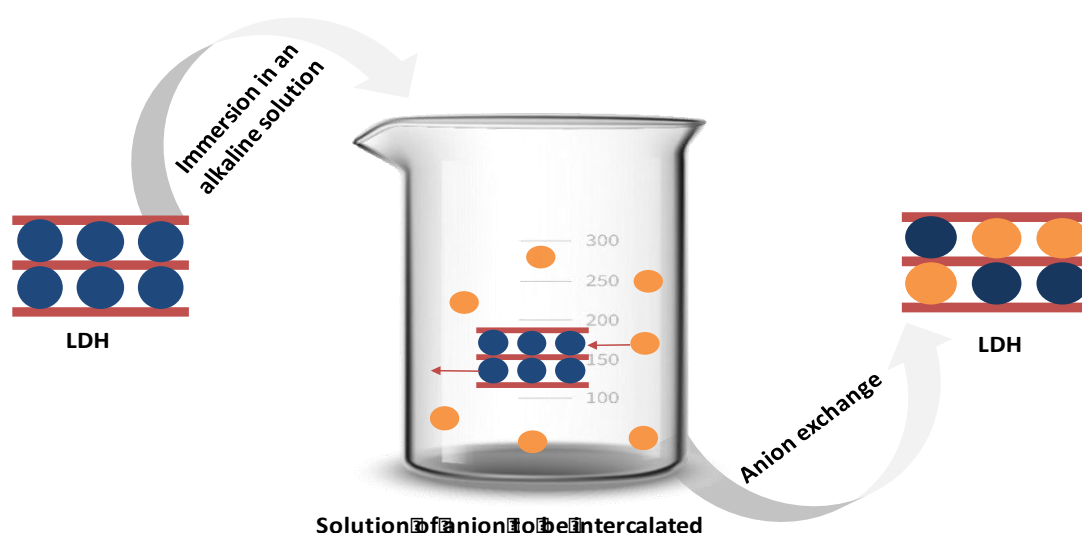
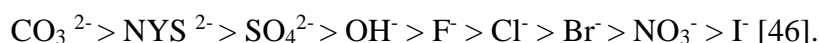


Fig.2. Schematic illustration of anion exchange process applied to LDH synthesis.

2.1.3. Reconstruction method

LDHs can also be synthesized by the reconstruction method known as a memory effect method. This method consists of the calcination of LDHs at mild temperature (400-500°C) to remove the

interlayer water molecules, hydroxyl groups of LDHs and intercalated anions, resulting in mixed metal oxides. Among other things, the regeneration of these mixed metal oxides is possible when they are exposed to water or any other solution of anions to be intercalated (Fig. 3). Additionally, this is very effective technique, especially for the synthesis of LDHs intercalated with organic molecules and many different anions to fulfill specific application requirements. Numerous LDHs have been synthesized via reconstruction route. Huo et al. [47] have synthesized the Zn-Al LDHs with different single anion intercalated (OH^- , CO_3^{2-} , MoO_4^{2-}) using simple and effective calcining and reconstructing routes. The results suggested that the materials obtained by these approaches achieved a good ability to activate NO and O_2 for increasing the photocatalytic NO oxidation efficiency. Zhang et al. successfully fabricated modified LDH with phosphotungstic acid through reconstitution method [48]. Lopez et al. [49] compared reconstruction and co-precipitation methods for the preparation of Mg-Al LDHs intercalated with Vancomycin, then evaluated their ability to controlled release of the drug. They showed that reconstruction samples resulted in particles with a heterogeneous chemical composition different from the prepared samples via co-precipitation route which were homogeneous. However, they exhibited higher drug content than coprecipitation samples. Haraketi et al. [50] reported the intercalation of salicylic acid into Cu/Al-LDHs by reconstruction reaction method. The results confirm that LDHs can be useful to trap pharmaceutical compounds in order to maintain their therapeutic activity and reducing their toxic effects.

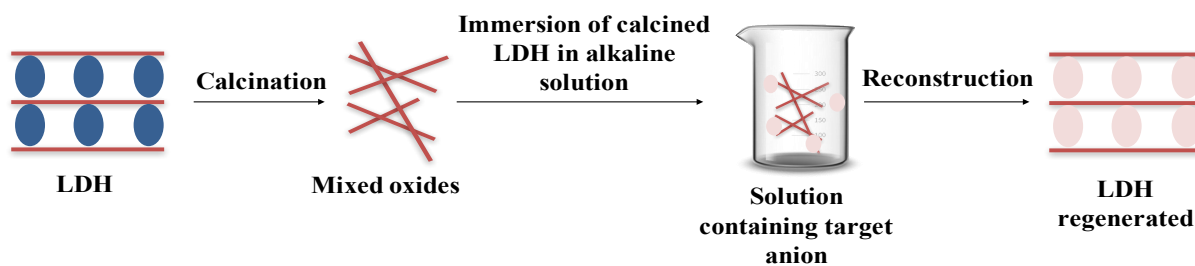


Fig.3. Schematic illustration of memory effect phenomenon for reconstruction of LDHs.

2.1.4. Hydrothermal technique

In addition to the above mentioned methods, hydrothermal is also a commonly used technique for the preparation of LDHs [51][52][53][54][35]. This method has been shown to be effective because it's useful to enhance the dissolution of hydroxide precipitate and the subsequent crystal growth (Fig.4). Furthermore, using hydrothermal process as additional treatment of other synthesis methods makes it more efficient, it yields the increase of particle size, purity and the higher LDHs crystallinity[38]. This is due to preparation conditions, LDHs crystallinity can be significantly affected by synthesis temperature and the time of hydrothermal treatment

[55]. Karami et al. [56] used Zn-Al-NO₃ layered double hydroxide, synthesized with hydrothermal method, to be incorporated into epoxy resin. They illustrated that Zn-Al-NO₃ LDHs assisted epoxy heat release in a shorter curing temperature interval with respect to the blank epoxy system whatever heating rate. Khataee et al. [57] successfully fabricated Ni-Fe-LDHs/rGO nanocomposite through facile hydrothermal procedure. They scrutinized this material for the degradation of moxifloxacin (MOX), as a model emerging contaminant. The outcomes of this study revealed that the synthesized Ni-Fe-LDHs/rGO nanocomposite is an effective solid to treat environmental pollutants.



Fig.4. Schematic representation of the synthesis hydrothermal process of LDH.

2.2. Non-conventional routes for the preparation of LDHs

2.2.1. Sol-gel method

The sol-gel process gives a new and interesting route to the construction of highly pure and homogeneous nanomaterials such as metal oxide nanoparticles in addition to mixed oxide materials [1]. Owing to the biggest advantage of sol-gel method, which leads to produce large surface mesoporous nanoparticles and allows to an excellent control of the reaction process [58]. It could be more effective approach employed to synthesized LDHs (Fig.5) [59] [39] [60]. This technique is required in case of insoluble salts using an alternative solvent, which can render such materials soluble [61]. The advantage of using sol-gel synthesis process is high homogeneity, high reproducibility, high quality and the possibility to enhance the particle size, the morphology and surface area of the compounds. This is can be performed by variation of several parameters such as the composition of the aqueous solution, the pH, and the agitation time [62][63]. Several studies focused on the comparison between sol-gel approach and co-precipitation [39][64][65]. The LDHs samples prepared by sol-gel method showed a small size of the particles, high purity and high specific surface area than LDHs synthesized by co-precipitation process [60]. However, lower crystallinity on the structure of the prepared materials is considerably observed through this synthesis method [65]. These finding results

making the sol-gel route preferable than the other process. Some researchers studied the impact of used reactants, on the thermal stability of LDHs materials [39] [66] and another investigated the effect of different transition metal on the substitution of $Mg_{3-x}M_x/Al$ ($M = Mn, Co, Ni, Cu, Zn$) layered double hydroxides were prepared in citric acid and 1,2-ethanediol as complexing agents in the sol-gel processing [60]. The results showed that in the different LDHs samples successfully synthesized through sol-gel route, the surface properties and the morphology of the final products were significantly affected by the nature and the amount of transition metal.

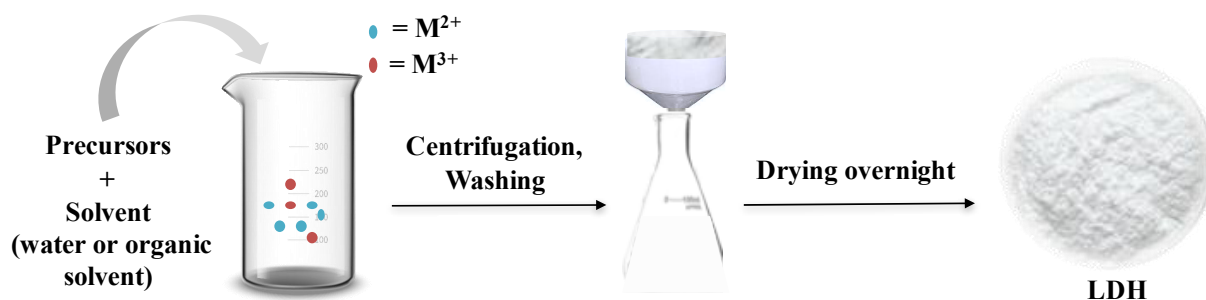


Fig.5. Schematic illustration of the sol-gel process applied to LDH synthesis.

2.2.2. Polyol method

The polyol method is one of the recent and successful synthesis processes to prepare different layered double hydroxides. If the polyol organic solvents like alcohol solvents are used as surfactant agents, it is termed as polyol route. This polyol process turned out to be important way for the preparation of composites such as oxides and layered double hydroxides, due to the simple operation, high homogeneity at the molecular level and no direct control of the pH [67]. Some metal cations are difficult to form layered double hydroxide by various methods, but the reaction is easier to occur in a polyol medium with high temperature. For constructing LDHs nanostructured, polyol method was employed in many studies [68][69]. Typically, suitable precursors are dispersed in solvent polyols and heated at a given temperature, and distilled water corresponding to a desired hydrolysis ratio is added to a solution of the precursor salt. After stirring, the mixture is filtered, washed with distilled water and once with ethanol, then, dried at a given temperature [70]. The choice of these conditions of hydrolysis ratio and temperature depend on the sample to be synthesized [68]. Prevot et al. [43] reported the synthesis of a composite of Ni-Al LDHs and Co-Al LDHs by a polyol method using ethylene glycol, diethylene glycol, or ethanol as surfactant agents. The results revealed that the crystallinity of the LDHs nanocomposite is not affected by the nature of organic surfactant, similar reflections of the final products are observed in the DRX patterns, regardless of the synthesis solvent. The samples prepared by inorganic polymerization in a polyol medium showed homogeneous pore size distribution and the highest BET surface area than those of

coprecipitated derivatives, using an organic solvent leads the change of the crystal growth and yields a very compact particle aggregation for the LDHs materials. The formation processes of LDHs materials by polyol medium is shown in Fig.6.

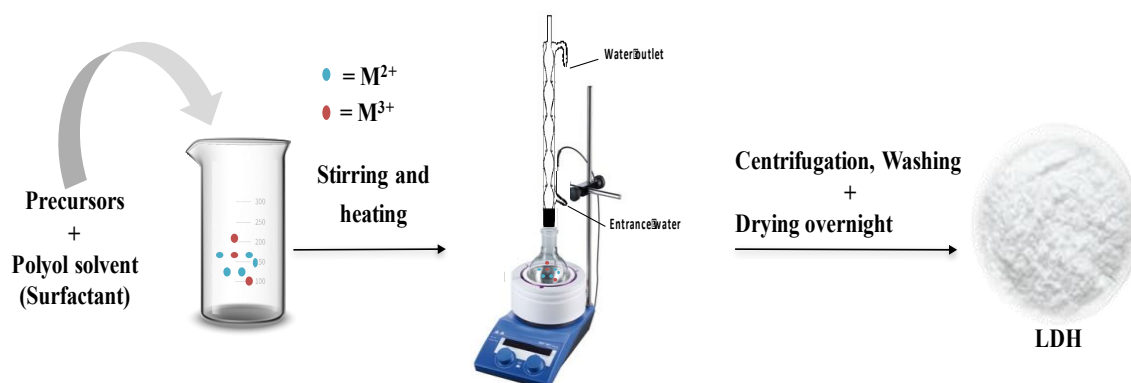


Fig.6. Schematic illustration of the synthesis polyol method of LDH.

2.2.3. Exfoliation/restacking and layer-by-layer assembly

More recently, exfoliation method attracted the attention of several researchers to prepare LDHs nanosheets [71][72][73]. This method is based on the process of swelling and delamination crystals or LDHs particles in order to produce separate nanosheets. The LDHs exfoliated can be directly prepared by selection of some solvents [74], owing to the exchangeable anions present in the interlayer space of LDHs to neutralize the positively charged LDHs lamination using ultrasound treatment to facilitate the exfoliation of the LDHs sample. Nanomaterials with high specific surface area and suitable pore size can be easily obtained from the exfoliated LDHs nanosheets. The exfoliation/restacking method has been effectively used for the synthesis of LDHs materials exhibiting high crystallinity and high homogeneity phase [75] [76], owing to electrostatic interactions between the LDHs and other components. Co-Al-LDHs /GO has been prepared by solid-phase exfoliation technique [77]. In this study, the finding results clearly reveal that the Co-Al LDHs-NS/GO-NS obtained is practically applicable for 2D materials in the asymmetric supercapacitors. On the other hand, the Ni-Fe LDHs/CB (carbon black) was synthesized through a ultrasonic exfoliation process for enhanced oxygen evolution catalysis [78]. The exfoliated Ni-Fe LDHs/CB exhibits high catalytic activity. The layer-by-layer assembly method is similar to exfoliation/restacking method for the preparation of LDHs nanocomposite [79][80]. The cationic surface was obtained by coating the substrate with polymeric solutions such as (diallyldimethylammonium chloride) (PDDA), poly (vinyl alcohol) (PVA), and poly (ethylene imine) (PEI) [81][77]. LDH/histidine/MnO₂ nanohybrids were synthesized by electrostatic self-assembly between 2D nanosheets of LDHs and δ -MnO₂

nanosheets in presence of zwitterionic histidine biomolecules [82]. The schematic illustration of exfoliation and assembly is shown in Fig.7.

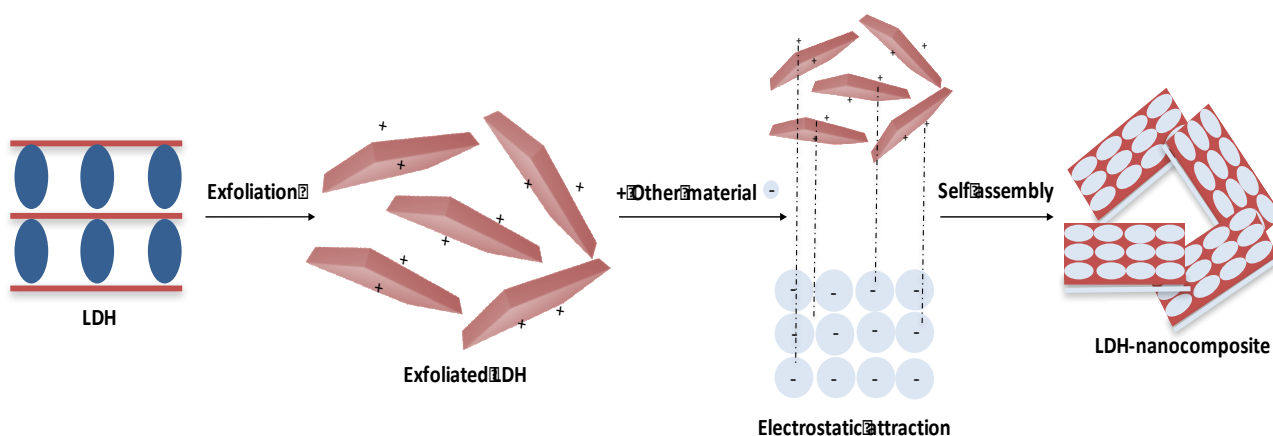


Fig.7. Schematic illustration of the synthesis exfoliation and self-assembly process of LDH nanocomposite.

2.2.4. Solvothermal and microwave techniques

These techniques are improved methods of the hydrothermal synthesis. Microwave irradiation is one of the most effective methods to prepare organo-LDHs in suitable solvent [83][84], due to its high controllability and low heat loss, with the advantages of shortened reaction time compared with traditional methods [85]. It was found that microwave assisted anion exchange provides decreased time in synthesizing organo-LDHs, and the resulting samples possess a high crystallinity. In the solvothermal reaction, nonaqueous solvents are used as agent intermediates in the synthesis reaction, replacing deionized water to dissolve the suitable precursors [86]. The Mg-Al LDHs has been prepared via solvothermal method in the appropriate solvent [87]. This synthesis process provides the opportunity for a facile route to highly delaminated high aspect ratio LDHs, which could be practically interesting as novel nanomaterials for energy conversion and storage.

3. Application of LDHs-derived Photocatalysts

Rational design of photocatalysts based LDHs structure with higher surface area may considerably improve the photocatalytic performance. On account of the unique properties of layered double hydroxides derived photocatalysts, they have been employed for several applications such as, photocatalytic degradation of organic pollutants, water splitting as well as antibacterial activity.

3.1. Photocatalytic degradation of organic pollutants

In recent years, a great number of persistent pollutants have been detected in wastewaters, which pose potential problems to human health and ecological environment. As a result, researches towards the development of eco-sustainable technologies for their

remediation are encouraged. Many studies have focused on the degradation of these pollutants from the environment [88][89][90]. In order to totally decompose this kind of contaminants, photocatalysis is used as a green and promising process [91][92][93][94]. The mechanism of photodegradation of organic pollutant is illustrated in Fig.8. Layered double hydroxides (LDHs) and their derivatives have demonstrated excellent photodegradation capability towards organic contaminants [95][96][97]. Zhang et al. [98], prepared Zn-Al- LDHs materials through hydrothermal method at constant pH, and tested their photocatalytic performances in the degradation of Rhodamine B. The results showed that the photocatalytic activity of Zn-Al-LDH was improved with increasing time synthesis on account of the enhanced crystal quality and the great separation of electron-hole pairs. Another study reported the synthesis of a series of Zn-Al- LDHs at different molar ratios ($r=1, 3$ and 5) [10]. These samples were prepared by co-precipitation technique and calcined at different temperatures. The finding results confirm that the photocatalyst obtained from the molar ratio of 3 and calcined at 500°C showed an excellent photocatalytic activity in degradation of caffeine as a model pharmaceutical pollutant. Additionally, few studies concentrated on the evaluation of photocatalytic performances of Zn-Ti-LDHs [99][100][101][102]. Chuaicham et al. [103] have studied the catalytic properties of Zn-Ti- LDHs synthesized by two methods (hydrothermal or reflux) in the degradation of phenol. A higher photocatalytic activity of the materials prepared by hydrothermal method was observed. This is due to the presence of amorphous ZnTiO_3 phase and the better heterojunction of electrons among ZnO , TiO_2 , and ZnTiO_3 . Other research has reported the photocatalytic performances of Ti-Ce/Zn-Al layered double hydroxides heterostructures in the photodegradation of an aqueous solution of phenol [104]. The Ti-Ce/Zn-Al LDHs materials shown an excellent photocatalytic degradation efficiency of phenol. The enhanced activity observed could be attributed to the presence of $\text{Ce}^{4+}/\text{Ce}^{3+}$ pair and to the presence of more photoactive species on the LDHs surface. On other hand, owing to the excellent surface properties of LDHs composites and derivatives, there are several studies on the photocatalytic performances of LDHs composites materials [105] [106][107]. Cai et al. [108] have studied the catalytic mechanisms in the degradation of Rhodamine B under visible light of prepared nanosized CdS/Co-Al LDHs. These solids were synthesized by combining methods of hydrothermal and anion-exchange method. The results show that the proposed photocatalyst has an excellent photocatalytic performance in degradation of organic compounds under visible light irradiation. Recently, Yazdani et al. [109] effectively synthesized g-C₃N₄-NiTi LDHs through hydrothermal process. They found that the photocatalytic performances of the g-C₃N₄-Ni-Ti LDH film is greater compared with pure Ni-Ti LDHs film and g-C₃N₄. Using these

synthetic g-C₃N₄-Ni-Ti LDHs films, the methyl orange degradation efficiency was 100 %. Similarly, the Ag/LDHs/g-C₃N₄ photocatalyst was prepared by hydrothermal process followed by photoreduction for the removal of aqueous Rhodamine B and 4-chlorophenol under visible light [110]. They demonstrated that prepared nanocomposites exhibited enhanced performance for the photocatalytic degradation of the proposed pollutants. In addition, Bing et al. [111] reported that Mg-Al-CLDHs/Bi₂O₃/Bi₂WO₆ heterostructures were prepared by a biotemplate route assisted with the hydrothermal route. The photocatalytic and adsorption characteristics of the prepared materials was studied for Congo red. Li et al. [112] prepared a novel ZnS / Zn-Al-LDHs photocatalyst via a mechanochemical process for the elimination of Rhodamine B under ultraviolet light illumination. The authors prove that the photocatalytic degradation performance under UV light showed a great evolution with increasing ZnS content, with 94% removal in 3 h using ZnS/Zn-Al-LDHs heterostructure, but only 75% by ZnS-free LDHs materials. More recently, Motlagh et al. [113] studied the fabrication of the novel Zn-Fe-LDHs/GO/GS nanocomposites through chemical co-precipitation method. Then, the as prepared Zn-Fe-LDHs/GO nanocomposites are coated on the glass support. In that work, they investigated the photocatalytic capacity of the prepared photocatalysts for the degradation of phenazopyridine hydrochloride, as model emerging contaminant, from the solution under visible light irradiation. The results revealed stability of synthesized photocatalyst during five cycles of photocatalysis. In another report, microwave hydrothermal method was investigated to prepare the Zn-In-layered double hydroxides (Zn-In-LDHs) [84] and then the Zn-In-layered double oxides (Zn-In-LDOs) was prepared by controllable calcination. The photocatalytic performances were explored by MB degradation under the simulated sunlight irradiation. The achieved results exhibited that the prepared Zn-In-LDOs had a high MB photocatalytic degradation efficiency, compared to pure ZnO and In₂O₃.

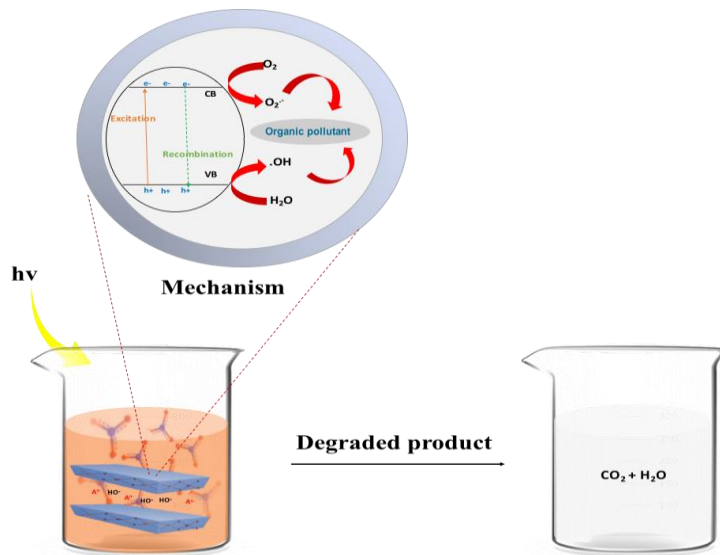


Fig.8. Proposed diagram of the charge transfer mechanism in a semiconductor initiating pollutant degradation in water.

Table 1. LDH based photocatalyst for organic molecules degradation.

Organic molecules	Photocatalysts	Synthesis methods	Main conditions	Degradation efficiency	Ref
Rhodamine B	Zn-Al-LDHs	Hydrothermal method	The photodegradation of RhB was performed by using 0.03 g of c-Zn-Al-LDHs-24-300 in 30 mL of RhB solution at a concentration of 2 mg/L. The finding results showed that this material exhibited an excellent photocatalytic activity under UV irradiation by using high-pressure mercury lamp (250 W, main emission wavelength of 365 nm) in 60 min.	94%	[98]
Rhodamine B	CdS/Co-Al-LDHs	Hydrothermal and anion-exchange	The CoAl/CdS-LDHs with molar ratio 1:2 showed a high photocatalytic performance for photodegradation of 100 mL RhB (1.0 mg) aqueous solution containing 100 mg of photocatalyst dose in 30 min and can be completely degraded after 60 min under visible light irradiation, using 500 W Xenon lamp. The high photodegradation efficiency of Rhodamine B can be attributed to the presence of CdS in the LDHs interface, which can enhance the electron-holes pairs separation.	72%	[108]
Rhodamine B	Ag/LDHs/g-C ₃ N ₄	Hydrothermal process	The photocatalytic performance of 50 mg Ag/LDHs/CN nanocomposites was evaluated in the photodegradation of Rhodamine B (200 mL, 5mgL ⁻¹) under visible-light by using a 300 W halogen lamp. The presence of Ag in the LDH material can be significantly improve the photodegradation of Rhodamine B during 30 min, which promotes transfer ability of photo-produced charge carriers.	99%	[110]
Rhodamine B	ZnS/Zn-Al-LDHs	Mechanochemical process	The photodegradation of 250 ml 4 mg/g Rhodamine B (RHB) under UV irradiation was achieved an excellent efficiency in 180 min by using 0.25 g2ZnS/Zn-Al LDHs heterostructure composite photocatalyst. This finding result attributed to the transfer of electrons from ZnS to LDHs, which leads to reduce photogenerated electron-hole recombination.	94%	[112]
Rhodamine B	Ni-Mn-LDHs/g-C ₃ N ₄	Solvothermal method	The photodegradation efficiency of Rhodamine B was performed by using Ni-Mn-LDHs/g-C ₃ N ₄ in the follows condition : 0.1 g of the catalyst was dispersed in 100 mL of RhB (50 mgL ⁻¹) under visible light irradiation by using Hg lamp ($\lambda > 420$ nm). The high photocatalytic	99%	[114]

phenol	Ti-Ce/Zn-Al/LDHs	Reconstruction	degradation efficiency of dye during ≤ 10 min can be attributed to the strong synergistic coupling of Ni-Mn- LDHs and g-C ₃ N ₄ . The Ti-Ce/Zn-Al-LDHs showed a high photocatalytic performance 250 min. The great photodegradation of phenol (20 mg/L) as emerging molecule by using 1.0 g/L Ce-Ti/ LDHs photocatalyst under UV and solar light irradiation (300 W Xenon lamp), due to the presence of ZnO phase in the LDHs material and a synergetic effect between TiO ₂ and CeO ₂ semi- conductors that enhances the photocatalytic activity of the hetero- structured semi-conductors.	95%	[104]
phenol	Ag ₂ CO ₃ /Mg-Al LDHs	Anion exchange process	The photocatalytic experiments present a high photodegradation efficiency of phenol. The Ag ₂ CO ₃ /Mg-Al-NO ₃ LDHs nanocomposites improved the photodegradation of this molecule (10 mg/L). 50 mg of photocatalyst was dispersed in 100 mL solution and examined under visible light irradiation (Xe light source). The excellent photocatalytic performance of this material after 60 min can be explained by wide-distribution of Ag ₂ CO ₃ nanoparticles on the surfaces of the 3D flower-like nanocomposites, which improved the photodegradation of organic molecules.	90%	[115]
caffeine	Zn-Al-LDHs	Co-precipitation	Photocatalytic experiments were carried out using a caffeine solution with an initial concentration of 20 mg/L and a catalyst dose of 0.3 g/L irradiated by using UV mercury lamp (400 W). The experimental results exhibit that the prepared photocatalyst was photocatalytically more effective than standard Degussa P-25 titanium dioxide after 210 min.	97.32%	[10]
caffeine	Ag-ZnO-La ₂ O ₂ CO ₃	Co-precipitation	The photodegradation of caffeine was achieved an optimum efficiency under UV-irradiation (mercury lamp (400 W)) within 40 min by using Ag-ZnO-La ₂ O ₂ CO ₃ in the follows conditions: 20 mg/L of caffeine solution and 0.3 g/L photocatalyst dose. The enhanced photocatalytic performance due to the interfacial heterostructure in the 5% AgZnO-Al ₂ O ₃ catalyst. The results show also that the photocatalyst showed a high stability in the photocatalytic performance.	99,4%	[116]
phenazopyridine hydrochloride	Zn-Fe- LDHs /GO/GS	Co-precipitation method	The photodegradation experiments were performed in 500 ml of PhP aqueous solution of PhP (15 mg/L, pH of 8 natural pH) by using Zn-Fe-LDHs/GO/GS. This photocatalyst showed a high photodegradation	93.95%	[113]

			efficiency in 150 min under visible light irradiation, using 10 W LED lamp ($\lambda \sim 400$ nm). The high photocatalytic performances could be due to the addition of oxidant ($K_2S_2O_8$) and the presence of more of reactive species photogenerated by the photocatalyst under visible light irradiation.		
Methyl orange	g-C ₃ N ₄ -NiTi-LDHs	Hydrothermal process	The result of the photocatalytic experiments showed an excellent photocatalytic activity of g-C ₃ N ₄ -NiTi-LDHs for the photodegradation of methyl orange (20mg/L) after 240 min under Vis-LED irradiation. This highest value of photodegradation efficiency due to low concentration of methyl orange pollutant, which can be adsorbed on the active sites of photocatalyst.	100%	[109]
Congo red (CR) and Doxycycline (DC)	Mg- Al-CLDHs/ -Bi ₂ O ₃ /Bi ₂ WO ₆	Biotemplate route and hydrothermal route	The photocatalytic activity of the Mg- Al-CLDHs/-Bi ₂ O ₃ /Bi ₂ WO ₆ was tested in a photodegradation of Congo red (CR) or Doxycycline (DC) solution (100 mg/L). The finding results show that the Bi ₂ O ₃ /Bi ₂ WO ₆ /Mg-Al-CLDHs heterojunction exhibits a superior photocatalytic activity toward both pollutants under sunlight irradiation (500 W Xenon lamp) in 60 min, this photodegradation efficiency due to the synergic effect and the high charge separation ratio of Bi ₂ O ₃ /Bi ₂ WO ₆ heterojunction and the presence of more of reactive species	71.43% of CR and 82.85% of DC	[111]
Methylene blue	MoS ₂ / Mg-Al LDHs	Exfoliation /self-assembly	The high photocatalytic performance of the MoS ₂ / LDHs composite toward Methylene blue dye (20 mg/L) after 180 min of irradiation time and by using 300 W xenon lamp as visible light source and 100 mg/L of photocatalyst dose, can be attributed to the high separation of pairs electrons-holes photogenerated.	96%	[117]
Methylene blue	Zn-Al-Ti-LDHs	Hydrothermal or reflux	The photocatalytic experiments study of the photodegradation of methylene blue dye solution of 10 ppm by using Zn-Al-Ti material under UV-125 W halogen lamp for 4h irradiation time, showed that the photodegradation efficiency achieved due to the reduction of photogenerated electrons –holes recombination.	82.07%	[100]

3.2. Antibacterial activity

LDHs derived photocatalysts have recently attracted great attention in biological field [118] [119]. The presence of the pathogen bacteria threat human health by causing a lot of severe diseases [120] [121] [122]. Therefore, it is necessary to ensure alternative methods that could inhibit bacterial growth. Various researches attempted to develop new antibacterial agents such as inorganic metal oxide nanoparticles prepared from LDHs as precursor [123][124][125].

The LDHs are cationic materials, which could adsorb to the negatively charged cell wall of bacteria gram negative through electrostatic interactions. Moreover, the large specific surface area of LDHs, improve their adsorption ability on the surface of these types of bacteria, which lead to the death or inhibition bacteria growth.

UV-visible light or any other irradiation source [126][127], could be considered another main contributor to the antimicrobial efficiency of candidates, which the semiconductors could produce ROS under irradiation, these ROS species lead to shatter membrane components and damages functional proteins and DNAs, resulting bacterial death. For example, Shang et al. [128] exhibited the photocatalytic antibacterial efficiency of the Fe₃O₄@PTAA-LDHs photocatalyst against *E. coli* and *S. aureus* under ultraviolet and visible light. The photocatalytic antibacterial activity of the photocatalyst showed 99.99% under solar irradiation. The high antibacterial activity may be attributed to the presence of OH[•] photogenerated. Bouaziz et al. [129], have studied the antibacterial activity of TCH-Zn₂Al-LDH and OXY-Zn₂Al-LDH toward *E. coli* negative Gram and *S. epidermidis* positive Gram under visible light and a UVA lamp. The results show that the antibacterial activity of the materials under was lower under UV than visible light irradiation. In addition, Geetanjali et al. [130] synthesized silver nanoparticles substituted Zn-Al LDHs through co-precipitation followed by calcination at 150°C. The antibacterial activity of these samples was evaluated against *Escherichia coli* and *Staphylococcus aureus*. The results exhibit that the calcined material achieves a stronger antibacterial activity towards these kinds of bacteria, and concluded that the high stability of the thermally treated LDHs can lead to its application in the field of ceramic industries. In another report [131], the antibacterial activity of Cu incorporated Zn-Al layered double hydroxide prepared via co-precipitation method and aged at a temperature range of 400-900°C, was evaluated against *Escherichia coli* (Gram negative) and *Staphylococcus aureus* (Gram positive). The finding results show that the LDHs materials and their calcined products exhibit higher and effective antibacterial performance against both Gram-positive and Gram-negative bacteria, due to high biocompatibility and chemical inertness of layered double hydroxides. On the other hand, Liu et al. [132] reported in their work, an ultrathin 2D composite fabricated by Zn-Al-Ti- LDHs nanosheets loaded with dehydroabietic

acid derivatives (DHADs). The achieved results exhibit high production capacity of prominent reactive oxygen species (ROS) under UV irradiation. In addition, in vitro and in vivo tests, achieved a superior antibacterial ability toward *E. coli* and *S. aureus* with biofilm inhibition rate of 94% and 91% respectively. The result confirmed that the material has great potential bactericidal applications. Moreover, Salguero et al. [25] successfully synthesized a hybrid composite films intercalated with ciprofloxacin using precipitation method at variable pH followed by dispersion of hyaluronan (HS) for obtaining hybrid films. In this research, they investigated antibacterial activity of the obtained photocatalysts against *S. aureus*. The interesting properties of this hybrid composite make them a promising material towards many bacteria. Additionally, Ni-La-LDOs/Fe₃O₄ were effectively prepared through a simple co-precipitation technique by Thanh et al.[133]. From the obtained results, it is clearly showed, that the proposed samples exhibit a high antibacterial activity toward *E. coli*, on account of the presence of Ni and La species, which could greatly improve the antibacterial performance of the Ni-La-LDOs/Fe₃O₄ composite.

Therefore, LDHs based photocatalysts and their calcined samples [134][135], possess a great potential in biological sectors (Fig.9), due to their low cost, low or null toxicity [136], higher surface area and catalytic properties. According to the literature, LDHs have been confirmed as promising inorganic antibacterial agents which could be practically employed in many technologically important fields such as pharmaceutical area [137] and biomedicine [138] by investing its antibacterial activity towards various bacterial strains.

We can observe from Table 2 that most publications concerning studies of antibacterial activity of LDHs based materials are focused on the disinfection of *E. coli* and *S. aureus* as pathogenic bacteria. From results on inhibition zone or bacterial growth, we can conclude that the materials exhibit approximately similar activities.

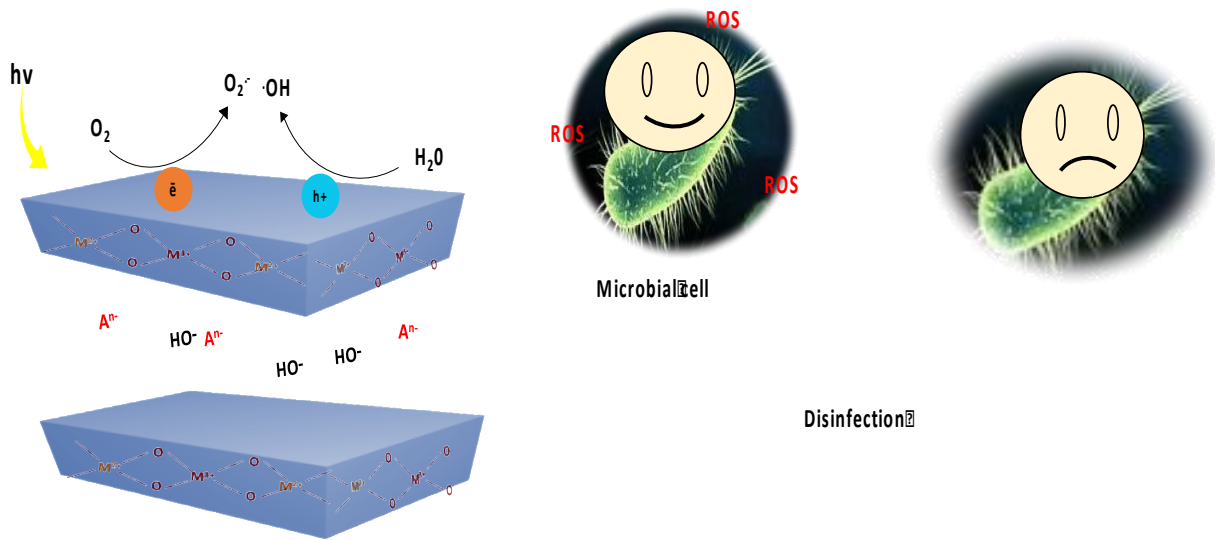


Fig.9. Schematic illustration of antibacterial activity of LDH based photocatalyst toward pathogen bacteria.

Table.2. LDH based photocatalyst for antibacterial activity.

Photocatalysts	Synthesis methods	Application	Inhibition zones or bacterial growth	Ref.
Zn-Al-LDHs	Co-precipitation	Antibacterial activity toward E. coli and S. aureus	15 mm and 38 mm, respectively	[118]
Zn-Al-BzDC- LDHs	Anion-exchange reaction	Antimicrobial test toward S. cerevisiae	40% inhibition Saccharomyces cerevisiae growth	[123]
DHAD/Zn-Al-Ti- LDHs	Series of reactions	Antibacterial ability toward E. coli and S. aureus	Inhibition rate against E. coli and S. aureus after 40 min of illumination reached 94% and 91% respectively	[132]
Ni-La-LDOs/Fe ₃ O ₄	Co-precipitation technique	Antibacterial activity toward E. coli	~104 CFU/mL E. coli was completely inactivated after 2 hrs contact	[133]
Nap/Mg-Al- LDHs	Calcination–reconstruction	Antibacterial performance toward E. coli, K. pneumonia, S. aureus, S. flexneri, S. cereus and P. aeruginosa	2.5, 5, 6, 3 mm, NI, and NI (not inhibition) respectively.	[139]
Zn-Al-MA- LDHs	Ion-exchange method	Antimicrobial activity against E. coli and S. aureus	15.64 mm and 18,52 respectively	[140]
LDHs@PPy-Ag	Chemical polymerization of pyrrole	Antibacterial performance against E. coli	100% inhibition growth	[141]
Ag@VB9-LDHs	Environmentally-friendly and green media extracted from Rosmarinus officinalis plants	Antibacterial activity against E. coli and S. aureus	11 mm and 19 mm, respectively	[142]
Mg-Cu-Al- LDHs	Co-precipitation method	Antibacterial activity against E. coli, S. aureus, P. aeruginosa, and E. faecalis	Between 15 and 28 mm for uncalcined and between 12 and 30 mm for calcined samples.	[143]

3.3. Water splitting

Recently, photocatalytic water splitting processes give a promising approach for energy supply storage applications [144]. The generation of H₂ and O₂ by water splitting is considered an important goal of many researches to develop renewable energy resources [145]. Therefore, it is necessary to develop some trending photocatalysts, which have high activity for the generation of O₂ and H₂ [146][147][148][149]. Several studies are focused on the development of the precious photocatalysts based materials for oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) for water splitting applications [150][151][152]. Model band structures of LDHs for oxygen and hydrogen evolution reaction is shown in Fig.10. Among semiconductor-based photocatalysts, LDHs could be promising candidates for oxygen evolution reaction and hydrogen evolution reaction owing to their high surface area, unique morphology, mixed composition and advantageous features. The OER and HER rate was significantly improved by using these kind of photocatalysts [153][154][155][156].

In addition, improving the OER activity and highest purity of H₂ generation in water splitting process require higher overpotential [157][158], which leads to enhanced oxygen releasing capacity for the OER photocatalysts. Therefore, it is necessary to increase the electronic transmission capacity and the number of active sites. CdS-pillared Zn-Cr-LDH nanohybrids prepared by an exfoliation-restacking route was investigated for H₂ production by photocatalytic water splitting process [159]. The results show that the obtained LDHs achieve a great potential in the practical applications of full hydrogen evolution. In other report-[160], Fe³⁺ into Mg/Al layered double hydroxide framework have been synthesized via co-precipitation method. The material proposed achieve great results, through the highest crystallinity and the suitable surface structure, which exhibit an excellent hydrogen evolution performance under visible light irradiation. Other authors focused on nitrogen doped gC₃N₄/Ni-Al layered double hydroxides by using a one-step in situ hydrothermal reaction [161]. Photocatalytic performance of the material synthesized was investigated for hydrogen production under simulated light irradiation. This work demonstrates that gC₃N₄/Ni-Al-LDHs, due to the formation of 2D/2D heterojunction, which lead to high electron-hole separation photogenerated. The prepared material could be an emerging alternative for hydrogen energy production in water splitting, and may provide many advantages in catalytic fields, this can make them more employed in remediation wastewater. Moreover, Li et al. [162] synthesized Ni-Ti-LDH/RGO through in situ growth method. The obtained material was evaluated in water splitting under visible light for oxygen evolution reaction. The finding results show that Ni-Ti-LDH/RGO composite achieved an excellent oxygen evolution performance, which could be used as a promising photocatalyst in solar energy

conversion. Similarly, Co-Fe LDH have been shown an excellent photocatalytic performance toward oxygen evolution under visible light irradiation. The finding results demonstrated that the prepared photocatalyst achieved oxygen 45 $\mu\text{mol}/3\text{ h}$ production in the presence of AgNO_3 as an electron scavenger [163].

Qiao et al. [164] have investigated the synthesis of $\text{Co@CoO}/\text{NG}$ via in situ preparation process. The obtained material exhibits an excellent photocatalytic oxygen and hydrogen evolution, which achieved production rate 543198 $\mu\text{mol g}^{-1}\text{ h}^{-1}$ and rate $\mu\text{mol g}^{-1}\text{ h}^{-1}$ respectively.

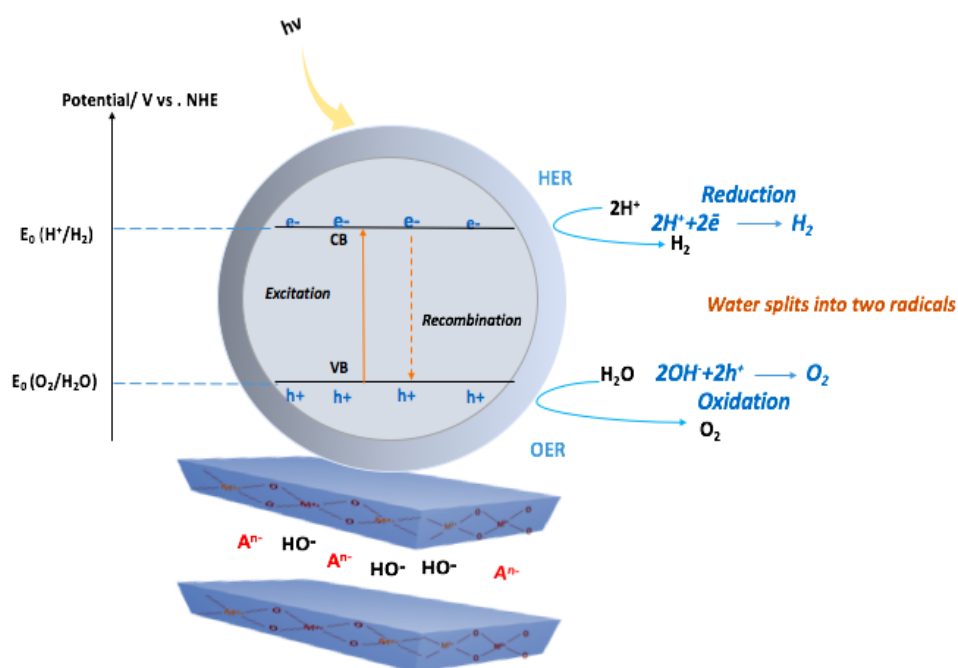


Fig.10. Schematic illustration of photocatalytic water splitting mechanism.

Table 3. LDH based photocatalyst for water splitting

Photocatalysts	Synthesis methods	Main conditions	Production rate	Ref.
ZnCr ₂ O ₄ @ZnO/g-C ₃ N ₄	in situ method	In order to evaluate the photocatalytic O ₂ and H ₂ evolution performances of the ZnCr ₂ O ₄ @ZnO/g-C ₃ N ₄ , an appropriate dose of photocatalyst was dispersed in 20 mL of aqueous solution containing methanol and AgNO ₃ as sacrificial agent. The photocatalytic reactions were carried out in a batch reactor under visible light by using 125 W visible lamp and 1 M NaNO ₂ solution as a UV filter. The finding experiments shown an apparent H ₂ and O ₂ production efficiency, owing to the synergistic effect between g-C ₃ N ₄ (Lewis base) and Zn ^{II} ions (Lewis acid).	H ₂ (847 μmole/2h) and O ₂ (455 μmole/2h) production	[165]
CdSe/Zn-Cr-LDH nanohybrids	mixing the suspensions containing cationic ZnCr-LDH nanosheets and anionic CdSe nanosol	The photocatalytic activity of CdSe/ZnCr-LDH nanohybrids was performed by hydrogen evolution from water splitting under visible light irradiation by using 300 W Xe lamp. 100 mL aqueous solution of 0.1 M Na ₂ S, 0.1 M Na ₂ SO ₃ as sacrificial agents and 50 mg of photocatalyst. The results demonstrated that the prepared photocatalyst exhibits a highest photocatalytic hydrogen production, attributed to the e self-assembly synthesis method.	2196 μmol h ⁻¹ g ⁻¹	[166]
Mg-Al-LDH/NiS	hydrothermal and precipitation methods	The photocatalytic performance of MgAlLDH/NiS for hydrogen evolution from water splitting was examined in the following conditions: 40mL aqueous methanol solution containing 40mg of the prepared sample was irradiated by using 300 W Xe-lamp (CEL-HXF300, AuLight, Beijing). The superior performance of MgAlLDH/NiS is mainly due to the presence of NiS, which improves the visible-light absorption and avoid the photo-produces charges recombination.	35.8 μmol h ⁻¹	[167]
CeO ₂ (5%)/Mg-Al-LDH	coprecipitation and hydrothermal routes	The photocatalytic activity of CeO ₂ (5%)/MgAl-LDHs was evaluated by hydrogen generation under visible light irradiation, using a 125 W medium pressure Hg lamp (420 nm) and 1 M NaNO ₂ solution as UV filter. The photocatalytic experiments showed that the CeO ₂ (5%)/MgAl-LDHs can be considered as effective photocatalyst for hydrogen production from water oxidation and exhibits.	f 990.0 μmol 2 h ⁻¹	[168]
gC ₃ N ₄ @pDA/Ni-Co-LDH	hydrothermal and calcination synthesis	In the aim to evaluate the photocatalytic performance of gC ₃ N ₄ @pDA/NiCo-LDHs photocatalyst, the experiment was performed at closed system, using using a 300 W Xe-lamp as visible light source. 50mg of sample was added to	1555.1 μmol h ⁻¹ g ⁻¹	[169]

		100mL of 20% vol.% TEOA and H ₂ PtCl ₆ ·6H ₂ O (Pt, 3 wt.%) aqueous solution. The highest photocatalytic performance of gC ₃ N ₄ @pDA/NiCo-LDHs toward H ₂ evolution due to the spatial separation of electron-holes photogenerated.		
CdS/Ni-V LDH	physical mixing process	The photocatalytic activity of CdS/Ni-V-LDHs was tested by using 5 W LED white light for hydrogen evolution, an appropriate amount of photocatalyst was dispersed in 30 mL solution of Na ₂ S and Na ₂ SO ₃ . The photocatalyst exhibits an exceptional photocatalytic hydrogen evolution from water splitting under illumination, due to the more efficient energy transfer.	478.96 μmol in 5 h	[170]
(Ni-Fe-P)	solvothermal synthesis	The photocatalytic characteristics of Ni-Fe-P was investigated by oxygen production under visible light irradiation. The experimental results shown that the Ni-Fe-P photocatalyst exhibits high photocatalytic oxygen evolution efficiency, which achieved an excellent production rate.	23.66 μmol s ⁻¹ g ⁻¹	[171]
Ni-Ti- LDH nanosheets	reverse microemulsion method	The photocatalytic activity of the NiTi-LDHs was examined by monitoring the time-dependent photocatalytic O ₂ production under visible irradiation (λ > 400 nm) using AgNO ₃ solution as a sacrificial reagent. The finding results display that the NiTi-LDH photocatalyst exhibits a better photocatalytic activity.	~2,148 μmol g ⁻¹ h ⁻¹	[172]
MoS ₂ /Co-Al LDH hybrid	Hydrothermal method	The photocatalytic hydrogen evolution was examined under visible light by using a 300 W Xe-lamp as irradiation source of 80 mL of aqueous methanol solution containing 50 mg of photocatalyst. The S-scheme Heterojunction MoS ₂ /Co-Al-LDHs was used as an effective candidate for hydrogen production from water splitting. The experiments results show that the obtained photocatalyst enhances the photocatalytic hydrogen production efficiency due to the unique 2D/2D architecture and ameliorative H* adsorption, which can be used as a promising photocatalyst in the field environment.	17.1 μmol·g ⁻¹ ·h ⁻¹	[173]
Cu ₂ O@Zn-Cr-LDH	Isitu route	The photocatalytic performance of Cu ₂ O@ZnCr-LDHs was evaluated in overall water splitting through visible light radiation without any sacrificial agent. The highest photocatalytic oxygen and Hydrogen production efficiency was observed for the obtained photocatalyst. These finding results attributed to the presence of the S ₂ O ₃ ²⁻ group in the gallery of ZnCr-LDH, which acts as an effective accelerator of the immigration of photo-induced charges.	H ₂ and O ₂ production rate of 0.90 and 0.44 μmol h ⁻¹ , respectively	[174]

4. Conclusion

This study reviews the synthesis routes of LDHs materials and their environmental applications. Traditional synthesis routes of LDHs, such as co-precipitation, hydrothermal, reconstruction and exchange-anion have been reviewed and compared. Indeed, the co-precipitation seems the most frequently used technique for the preparation of LDHs, due to its simplicity and low-cost chemicals. The hydrothermal techniques have been also applied to the synthesis LDHs, leading to highly crystalline materials with uniform morphology compared to co-precipitation technique. Additionally, anion-exchange is the frequently and inexpensive process to intercalate large sized anions between LDHs laminations. Many researches have been focused on the development of modification methods of LDHs, on account of the trending applications of these materials. This work has also briefly summarized some of the current synthesis methods, namely, sol-gel, polyol medium, exfoliation, self-assemblage, solvothermal, and microwave process. These approaches have been devoted to prepare LDHs nanocomposites which are difficult to prepare by traditional methods or to improve morphologic properties and catalytic performance. LDHs-derived were the promising choice for a several applications. They are considered to be promising photocatalysts for organic and inorganic pollutants remediation. In addition, the high generation of species actives of LDHs and their derivatives, makes them a promising antibacterial agent towards many pathogen bacteria in biological field. Furthermore, owing to high overpotential of these materials, they are considered as trends photocatalysts for O₂ evolution and H₂ production in water splitting. Hence, an extended review could provide a clear view in advanced photocatalysts materials. So, for the effective and extensive industrial applications, it is recommended to improve the performance of layered double hydroxides and their derivatives.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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none

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