

Review Article

Synthetic strategies of Layered double hydroxide 2D materials: A short review

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ABSTRACT

LDHs have received considerable research in the realm of transition-metal catalysis owing to their unique electronic and structural properties. More significantly, their applications in electro-catalysis such as splitting of water and production of dihydrogen from sustainable sources are remarkable. Moreover, during the last decade, their application has also been investigated in other fields of chemistry. This review intends to provide overview of synthetic strategies of LDHs in the last two decades.

Key words: Transition-metal catalysis, Layered double hydroxide, Electro-catalysis

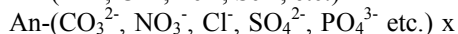
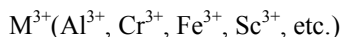
INTRODUCTION

Catalysis is undoubtedly an exciting field in chemistry and has played a significant role in the development of synthetic organic chemistry, pharmaceuticals, and other relevant fields of chemistry. By realizing the importance of catalysts in synthetic organic chemistry, in the last three decades, enormous efforts have been directed to develop high-performance catalysts and explored their application as catalysts in different organic reactions. Recently, concentrated attention has been focused on the development of catalysts based on low-cost transition metals and their application in the large-scale synthesis of value-added organic products. Of these, layered double hydroxides (LDHs) have gained considerable research interest due to their widespread application in numerous fields such as electro catalysis, material science, and transition-metal catalysis. Moreover, recently, LDHs were found application in the preparation of CO₂ adsor-

bents (Luet *et al.*, 2017; Luet *et al.*, 2017; Lvet *et al.*, 2019; Song *et al.*, 2014; Han *et al.*, 2015; Wang *et al.*, 2018), ion exchange hosts (Yu *et al.*, 2017; Liu *et al.*, 2014; Ma *et al.*, 2012), retardant additives (Zhitova *et al.*, 2019; Cai *et al.*, 2019), polymer / LDH nanocomposites (Huang *et al.*, 2019), drug delivery hosts (Liu *et al.*, 2019), and had also been applied as cement additives (Ma *et al.*, 2010). The major advantage of LDHs is that the structural and electronic properties of LDHs can easily be tuned by facile modification of their surface/interface structures.

LDH is considered a unique class of 2D material, comprised of cationic brucite-like layers, and has an interlayer region where charge compensating anions and solvation molecules usually reside. It can be represented by the formula $[M^{2+}_x M^{3+}_x (OH)_2]_{x+n} [A_n]_{x/n} \cdot 2H_2O$ where M^{2+} (Mg²⁺, Ni²⁺, Co²⁺, Fe²⁺, Zn²⁺, Cu²⁺ etc.)

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is normally 0.2-0.4. Metal cations prefer to reside at the center of edge-sharing the octahedral and OH⁻ occupy the vertex position and play a crucial role in the formation of 2D sheets. A fraction of octahedrally coordinated M²⁺ ions are replaced by M³⁺ ones resulting in a positive charge on the host layer. Moreover, the OH groups of the host layers are connected to the anion or H₂O molecule by H-bonds. For example, the crystal structure of MgAl–CO₃–LDH is shown in Figure.

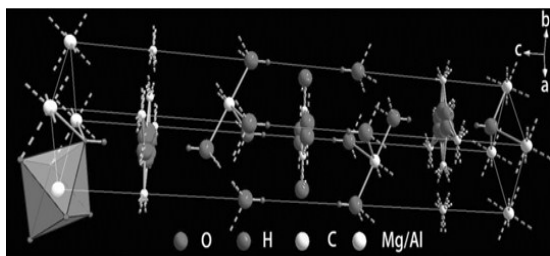


Figure 1. Schematic representation of the structure of MgAl–CO₃–LDH layered double hydroxide

In this review, we have highlighted the recent progress in the structure designing and exfoliation of LDHs and summarised various methods of preparation of LDHs nanosheets.

THE SYNTHETIC PROCEDURE OF LDHs

During the past few decades, considerable efforts have been directed to develop various procedures for preparing LDHs and exploring their potential in numerous fields. The synthetic methods of 2D LDHs can be broadly divided into two classes namely-the “top-down” and “bottom-up” approaches. Generally, the top-down method relies on physical shear force or chemical intercalation to achieve the interaction between adjacent layers which resulting mono or few-layered nanosheets. On the contrary, the bottom-up method depends on the direct preparation of 2D LDH nanosheets via chemical synthesis.

Direct synthesis or bottom-up method

The bottom-up approach is considered to be a suitable method for the direct synthesis of 2D nanosheets (Hur *et al.*, 2010). To this end, the various mechanical and chemical process that involves the application of laser beam on metals in aqueous solution, utilization of layer growth inhibitor in a microemulsion, and use of a special reactor to create a reaction environment, etc are the most notable.

PHYSICOCHEMICAL APPROACH

Pulsed laser ablation

Hur and co-workers, for the first time, introduced the pulsed laser ablation for the synthesis of LDH (Hur *et al.*, 2010). Interestingly, by applying this strategy, ultrathin nanosheets can be prepared without any chemical or heat treatment. The method is applicable for the synthesis of silver particles (Phuoc *et al.*, 2007), ZnO particles (Sasaki *et al.*, 2004), Au-Ag alloy (Kazakevich *et al.*, 2006; Compagnini *et al.*, 2008), and other stable phases depending on the properties of target materials and surrounding liquids. The method comprises two steps. First is the laser ablation of a metal target for trivalent cations in deionized water at room temperature using Q-switched Nd:yttrium aluminum garnet laser and the second is for bivalent source from the previously prepared trivalent metallic colloid by laser ablation over another metal target. Zn-Al, Co-Fe, Co-Al, and Mg-Fe were formed by controlling the ablation time, the wavelength to the thickness of the exfoliated 2D nanosheets. The lateral sizes of these LDHs are approximately 300, 100, 100, and 200 nm respectively. All these colloidal nanosheets were found to be stable without any formation of lamellar structure specially Mg-Fe and Co-Fe LDH layers have extremely large lateral sizes as compared to that of regular LDHs prepared on a TEM grid. TEM images of Mg-Fe LDHs showed a rolling and folding morphology with a thick-

ness of nearly 0.5 nm

Later on, Miller *et al.* applied pulsed laser ablation in liquid (PLAL) to synthesize a series of Ni-Fe LDHs with intercalated nitrate ion and water having formula $[\text{Ni}_{1-x}\text{Fe}_x(\text{OH})_2](\text{NO}_3)_y(\text{OH})_{x-y}\cdot n\text{H}_2\text{O}$ (Hunter *et al.*, 2014). Fe or Ni powder was firstly mixed in 10 mL aqueous metal nitrate solutions using a magnetic stirrer. For bimetallic LDHs, one type of metal was used as the ablation target and the nitrate salt of the other metal was dissolved in the precursor solution. Nanoparticles were formed by rapid cooling of a plasma consisting of the elements for the solid ablation target and the surrounding liquid. After the completion of the process, the LDH nanoparticle suspension was separated from the metallic ablation target using a strong magnet. By varying the ablation target, type of metal ions, and their concentration, as well as laser pulse energies, the composition of LDH with mixed metal, can be controlled. From powdered XRD measurement, it was found that iron-rich nanoparticles are poorly crystalline while the nickel-rich nanoparticles are more close to LDH structure. Mossbauer and X-ray absorption spectroscopic data indicated the incorporation of iron as Fe^{3+} to replace Ni^{2+} ion partially in Ni-Fe LDHs. TEM study indicates the lateral sizes ranged from ~ 7 -22 nm. This method is useful for the preparation of ultrathin LDH layers with a uniform size.

Microwave irradiation

Microwave irradiation is one of the most convenient methods to synthesize nanomaterials with uniform size. Xu and co-workers exploited this method to prepare Zn-Co LDH nanosheet which was found to be more convenient than the liquid exfoliation method (Qiao *et al.*, 2015). The aforesaid material was prepared by dissolving zinc nitrate hexahydrate, cobalt nitrate hexahydrate, and urea in deionized water and then transferred to a round-bottomed flask followed by microwave irradiation at 900 watts. XRD analysis

showed peaks at 003, 006, and 113 peaks which clearly indicate the presence of Zn and Co and it has been observed that the intensity of the peak increases with the increase of microwave power. Moreover, the AFM image disclosed that with an increase in reaction time, the lateral size increases. Peak-force-model atomic force microscopy (PF-AFM) study reveals that the thickness of the obtained nanosheets is ~ 2 nm

Chemical approach

Yan *et al.* devised a single-step method for the large-scale synthesis of Mg-Al LDHs (Yan *et al.*, 2012). To prepare this LDH, $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$, and urea were allowed to dissolve in 100 mL 30% H_2O_2 to yield a solution containing 0.01 M Mg^{2+} ion and 0.005 M Al^{3+} ion followed by heating at 150°C in Teflon tube for 24 hrs. After the required time, a translucent colloidal suspension was obtained. A closer inspection of reaction parameters revealed that the percentage of H_2O_2 has discernable effects on reaction yields. With an increase in the percentage of H_2O_2 the yield increases. Moreover, it has been observed that upon the addition of H_2O_2 , the 003 XRD peak shifted to a low angle which in turn indicated that the interlayer spacing of Mg-Al LDHs was expanded. Furthermore, on the increasing concentration of H_2O_2 to 30%, a semi-transparent colloidal suspension was obtained which can be kept for several weeks in the air without the formation of a precipitate. Finally, the author has analyzed the material with the help of scanning electron microscopy (SEM) which showed the hexagonal morphology of the Mg-Al LDHs with a size of 5-10 μm .

In a seminal work, Hu *et al.* developed a facile one-step synthesis of LDH monolayer in a reverse microemulsion (Hu *et al.*, 2006). The reaction involves $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ into an oil phase of isooctane with sodium dodecyl sulphate as surfactant and 1-butanol as co-surfactant. The pH of the solution was adjusted to 10 by adding NaOH. For the growth of

LDH, the aqueous phase containing the nutrients dispersed in the oil phase forms droplets surrounded by dodecyl sulphate groups. Both the diameter and thickness can be effectively controlled as the droplets provided limited space for the nutrients for the formation of LDH platelets. The XRD patterns of the gel-like materials presented two broad reflections at $2\theta = 7.5^\circ$ and 20° , while the strong basal plane Bragg's reflection of LDHs was missing indicating a lack of organized layered structure of the sample. Upon drying the pattern showed a gradual growth of a $2\theta = 3^\circ$ Bragg reflection suggesting that the sample gains some structural order. The AFM topology revealed an isolated oval object which has a uniform height distribution of around 1.5 nm and diameter distribution centered around 40 nm.

Chemical exfoliation of parent LDH crystals

Chemical exfoliation is another effective strategy to prepare 2D nanosheets from parent LDH crystals. The method provides scope for controlling the growth rate and chemical composition of LDHs and hence considered as one of the most convenient methods for the preparation of 2D nanosheets.

Synthesis of layered precursor compounds

The prime objective of the top-down process is to obtain multilayered parent compounds of high quality. It is a solution-based process to prepare LDH crystal and may be classified as coprecipitation, homogeneous precipitation, and topochemical oxidation. Coprecipitation involves the precipitation of a solution containing divalent and trivalent metal salts under alkaline conditions or at constant pH, e.g. by adding sodium hydroxide or sodium carbonate (Reichle *et al.*, 1986; Ehlsissen *et al.*, 1993; Xu *et al.*, 2001). Homogeneous precipitation usually utilizes a reagent such as urea or hexamethylenetetramine (HMT) and serves as a source of the alkaline medium as upon hydrolysis of these release ammonia at a controlled rate. This method generally leads to high crystallinity LDHs due to the

homogeneous nucleation procedure (Nobuo *et al.*, 2004; Cai *et al.*, 1994), whereas the topochemical oxidation process involves a topochemical oxidative intercalation starting from brucite like divalent metal hydroxide (Bitsianes *et al.*, 1955). Ma *et al.* (Ma *et al.*, 2007) introduced a new process of synthesizing transition metal bearing LDHs brucite like Co^{2+} - Fe^{2+} hydroxides by using $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ via HMT hydrolysis under a nitrogen atmosphere. By applying a topochemical approach the product was then transformed to $\text{Co}_{2/3}\text{Fe}_{1/2}(\text{OH})_2$ LDH by intercalation with I_2/CHCl_3 . On filtration and rinsing with anhydrous ethanol repeatedly a brownish product was obtained. The topochemical process was also used to prepare Co^{2+} - Co^{3+} LDH which cannot be prepared by the previous two methods as there is no stable dissociated Co^{3+} or $\text{Co}(\text{OH})_3$ in an aqueous solution (Ma *et al.*, 2008).

Lee *et al.* developed a novel synthesis of hydrotalcite-like Co^{2+} or Ni^{2+} - Fe^{3+} LDHs using a one-pot topochemical oxidation route where anthraquinone-2-sulphonate anions (AQS2) served as a mild oxidant and helped the oxidation of Fe^{2+} into Fe^{3+} to form the LDH phase and were intercalated into the interlayer space of the LDH during slow precipitation (Lee *et al.*, 2012). Another way is the refluxing CoCl_2 or NiCl_2 - FeCl_2 -AQS2-HMT solution with a stoichiometric ratio 2:1 of Co or Ni/Fe under nitrogen atmosphere for three hours. A brown and dark yellow solid precipitate was obtained for the Co-Fe LDHs and Ni-Fe LDH respectively. The average lateral size of both samples was found to be 0.5 μm and the thickness was around 70 nm. The diffraction peaks of XRD patterns showed a hydrotalcite-like phase similar to those in a Co-AQS2-LDH phase (Lee *et al.*, 2009).

Ion intercalation/exchange

Ion intercalation/exchange is another convenient method for synthesizing LDH with the desired ion and can regulate the properties of materials (Ma *et al.*, 2016., Wang *et al.*, 2009., Sene *et al.*, 2015; Ma *et al.*, 2017). As counter

ions are used to balance the parent layered change, ion intercalation occurs spontaneously. A plethora of organic molecules like glucose (Lv *et al.*, 2016), carbon dots (Liu *et al.*, 2017), and ethylene glycol (Wang *et al.*, 2016) can also be intercalated in addition to inorganic anions like alkoxide, molybdate, polyoxometallates, etc. Intercalating ions between LDH host layers expand the interlayer spacing for convenient transport of ions/electrons and also facilitate the subsequent exfoliation of LDHs into ultra-thin nanosheets (Liu *et al.*, 2006).

Exfoliation

Monolayered or few-layered nanosheet-shave drawn considerable interest in catalysis and have made many breakthroughs in synthetic organic chemistry and electro-catalysis. The formation of monolayered or few-layered nanosheets can be achieved through exfoliation of bulk LDH with weak interlayer forces which increase catalytically relevant active sites of the material. Therefore, in the last few years, the great impetus has been given to the development of efficient methods for the exfoliation of bulk LDH. Of these, soft chemical exfoliation and plasma exfoliation are the most notable.

Soft chemical exfoliation in liquid/solvent

Adachi-Paganoet *et al.* (Adachi-Pagano *et al.*, 2000) presented an elegant method for the exfoliation of LDH by preparing dodecylsulphate (DS-) intercalated Zn^{2+}/Al -DS—LDH and tried delaminating it in various organic solvents. They found that the LDH could be exfoliated in butanol, pentanol, and hexanol and remains stable for a long time. Zn^{2+}/Al -DS—LDH can be partially delaminated in other solvents such as water, methanol, ethanol, propanol, and hexane. Thereafter, Venugopal *et al.* had successfully applied such an exfoliation method to different types of divalent and trivalent LDHs including Mg-Al LDHs, Ni-Al LDHs, and Zn-Al LDHs intercalated with sodium dodecylsulphate or sodi-

um dodecyl benzene sulphonate (Venugopal *et al.*, 2006). The author has demonstrated that higher exfoliation yield can be achieved by lowering M^{2+}/M^{3+} in LDHs and they have also revealed that solvent plays a significant role during the exfoliation process. They have reported that alcohols such as 1-butanol, 1-octanol are the best solvent for the exfoliation of the aforementioned LDHs.

Besides alcohol, a non-polar solvent, toluene was also found to be suitable dispersant of DS- intercalated LDH (Naik *et al.*, 2011). On stirring in toluene and sonicating for 5 minutes, DS- intercalated $Mg_{0.67}/Al_{0.33}$ LDH and $Co_{0.67}/Al_{0.33}$ LDHs were rapidly exfoliated into monolayers with a clear transparent dispersion showing a clear tindal scattering effect. The whole mechanism was based on molecular dynamics simulation. The treatment with the solvents disrupts the Van-der Waals force between chains linked to adjacent host layers for the LDH having long-chain surfactant molecules. Thus, DS- converted the hydrophilic LDHs into hydrophobic which promotes solvation with non-polar solvents such as toluene.

Hibino and Jones, for the first time, reported creating a desirable interlayer environment to perform liquid exfoliation in formamide (Hibino *et al.*, 2001). For this purpose, different amino acid anions including glycine, serine, and L-aspartic acid were allowed to insert in the galleries of Mg_n/Al_k -LDHs, and polar solvents like water, ethanol, acetone, formamide, ethylene glycol, and diethyl ether, are used as dispersants. The study disclosed that glycine and formamide combination provides the best result. The author has noticed that upon mixing 0.03 g Mg_3/Al -glycine LDH in 10 mL formamide under stirring conditions, rapid exfoliation occurred in a few minutes. They also studied Mg-Al LDHs with various amino acids to create an interlayer suitable for solvation of formamide that could break the H-bonding network and helps in delamination.

Delamination of Co-Al LDHs in formamide was studied by Liu *et al.* (Liu *et al.*, 2006) to prepare hexagonal Co-Al-Co₃ LDH platelets of 4 μm in lateral size by following the urea method. It was then converted to Cl⁻-LDH by treating with a NaCl-HCl mixed solution (Iyi *et al.*, 2008). Later by an anion exchange process with salts like NO³⁻, ClO⁴⁻, acetate, lactate, dodecylsulphate, and oleate, Co-Al LDHs intercalated with anions. 0.1 g of the latter was then mixed with 100 mL formamide and agitated vigorously in a mechanical shaker at a speed of 160 rpm for two days. A pink transparent suspension was obtained containing a nanosheet with a lateral size upto 2 μm . AFM showed a flat morphology with an average thickness of ~ 0.8 nm which can be explained as the sum of the crystallographic thickness of the LDH layer (0.48nm) and an absorbed monolayer of formamide molecules (~ 0.3 nm) (Li *et al.*, 2005) indicating the unilamellar structure of the exfoliated nanosheets.

Synthesis of Co-Ni LDHs from brucite like Co-Ni hydroxide with bromine as an oxidizing agent was reported by Liang *et al.* A variety of inorganic and organic anionic forms of Co-Ni LDHs were prepared by the subsequent ethanol assisted anion exchange process. By varying the Co-Ni ratio different colors can be inserted into translucent suspensions of nanosheets. Delamination of LDH could be possible in an aqueous solution as reported by Iyi and co-workers. They added aqueous zwitterion solution into ClO⁴⁻ intercalated Mg-Al LDH and successfully obtained transparent colloidal suspension (Iyi *et al.*, 2013).

Monohara *et al.* (Manohara *et al.*, 2010) prepared formate intercalated Ni-Al LDHs by formamide hydrolysis which could be delaminated in water. Osmotic swelling of the formate ion in water leads to the exfoliation of the metal hydroxide layers into lamellar particles. This is a green alternative to the traditional exfoliation method using organic solvents. However, the incorporation of anions with high hydration enthalpy in the interlayer of LDH leads to a loss in en-

thalpy.

Partial delamination in dimethyl sulphoxide and N-methylpyrrolidone was studied by Zhao *et al.* (Zhao *et al.*, 2011). LDH with nitrate ions intercalated with organic molecules with an average thickness of the platelets ~ 13.2 nm can be partially exfoliated in DMSO. AFM study revealed the thickness of the LDH platelets decreased to 1.8 to 5.3 nm during delamination. They also reported that N-methylpyrrolidone (NMP) leads to the formation of transparent LDH suspension. The mechanism of exfoliation of LDHs using DMSO and NMP was similar to that of formamide.

Plasma exfoliation

During the last decade, the concept of plasma exfoliation, introduced by Langmuir, has emerged as a powerful idea in the realm of material chemistry and has gained considerable research interest recently (Langmuir *et al.*, 1928; Shim *et al.*, 2016; Wang *et al.*, 2013; Girshick *et al.*, 1989; Moshrefi *et al.*, 2018; Mangolini *et al.*, 2005). This technology was used to exfoliate layered compounds including graphite (Wang *et al.*, 2017), black phosphorous (Lu *et al.*, 2014), and LDHs (Wang *et al.*, 2017). The plasma helps to cleave the interlayer anions and diminished the interaction between the host layers resulting in exfoliation and simultaneously it creates multivacancies in exfoliated LDH sheets. Wang *et al.* exploited this method for the exfoliation of ultrathin Co-Fe LDH nanosheets. Later on, they used N₂ plasma to exfoliate the bulk Co-Fe LDHs into ultrathin nanosheets (Wang *et al.*, 2018). To achieve this outcome, they first prepared Co-Fe LDHs by hydrothermal reaction followed by treatment of N₂ plasma for 60 minutes. With the help of different analytical techniques, they showed the successful exfoliation of Co-Fe LDHs and the formation of ultrathin nanosheets with numerous atomic-sized holes having more exposed edge sites.

CONCLUSION

In this article, we have tried to present a brief overview of recent developments in the synthesis of LDH nanosheets. Generally, these approaches can be broadly divided into two classes namely bottom-up and top-down strategies. We have put efforts to incorporate the current literature which describes the synthesis of LDH nanosheets using both bottom-up and top-down strategies. Within the short span of time, considerable development in the field has been witnessed. In our view, LDHs will be an emerging area of research in the near future as they are chemically precise materials that can offer chemists, biologists, and materials scientists a new avenue for research exploration.

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