

# Layered Double Hydroxides/Polymer Nanocomposites

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**Abstract:** Layered double hydroxides (LDH) are a class of ionic lamellar compounds made up of positively charged layered hydroxides with an inter layer region containing charge compensating anions. LDH can be introduced as precursor into polymer matrix to prepare LDH / polymer nanocomposites. The properties of the polymer matrix can be strengthened as the addition of LDH, and nanocomposites have shown excellent performances and development potentials in many fields. In this paper, the preparation methods of LDH / polymer nanocomposites are reviewed, such as blending, intercalation, in-situ, exfoliation / adsorption, layer-by-layer (LBL) assembly. Then the applications of the LDH/polymer nanocomposites are also summarized, such as flame retardant, gas barrier, infrared absorption, controlled release, adsorption. Finally, development trends of research direction and research field of the LDH / polymer nanocomposites are prospected.

**Keywords:** layered double hydroxides; polymer; nanocomposites; preparation methods; application and properties

## 1. Introduction

With the continuous improvement of human needs, traditional single-component materials can no longer meet the needs of socio-economic and technological development. Combining two or more different materials is an important way to develop high performance materials. The combination of inorganic particles and polymers can perfectly combine the rigidity, dimensional stability, thermal stability and the like of inorganic materials with the toughness, process formability and dielectric properties of polymers, and thus attracts extensive attention of researchers<sup>[1]</sup>.

Layered double hydroxides (LDH) are a class of layered compounds composed of negatively charged anions (inter layer anions) and positively charged metal hydroxides (main body sheets), first in 1842. Discovered by Swedish scientist Circa<sup>[2]</sup>. In 1942, Feitknecht *et al.* first reacted a metal salt solution with an alkali metal hydroxide to obtain LDH, and proposed a two-layer structure model of LDH until its layered structure was verified in 1969<sup>[3]</sup>. The structure of LDH and the inter-layer object are adjustable, and it has the advantages of high ion exchange capacity, low production cost and less pollution, so its application is very extensive. By introducing LDH into the polymer, a polymer-based composite material having different functions and structures can be obtained, and LDH can enhance or improve the functionality of the polymer matrix. A functional composite film mainly composed of LDH can also be obtained by a layer-by-layer self-assembly method, and the polymer also plays an important role therein. The combination of polymer and LDH produces a synergistic effect, and the composite exhibits superior physicochemical properties over a single component. It has broad application prospects in the fields of light, electricity, magnetism and chemistry. This paper mainly introduces the preparation method of LDH/polymer nanocomposites and its important role in many fields in recent years.

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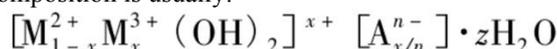
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## 2. Structure and properties of 2LDH

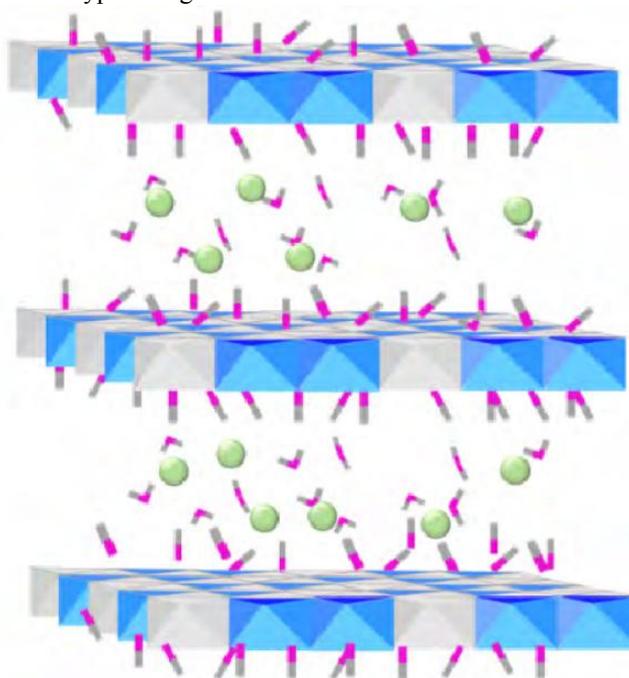
### 2.1 Structure of LDH

LDH is a three-dimensional crystal structure formed by longitudinally ordering two-dimensional layers of nanometer-scale laminates. The laminate consists of hydroxides of divalent and trivalent metals, and the anions between the layers are electrostatically attracted, hydrogen bonded, ionic bonded, etc. The way is connected to the main board. The layer skeleton has a positive charge, and the interlayer anions are balanced with it, and the whole body is electrically neutral. Its chemical composition is usually:



M<sup>2+</sup> is a divalent metal ion on the plate layer, including Mg<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup>, etc.; M<sup>3+</sup> is a trivalent metal ion on the plate layer, including Al<sup>3+</sup>, Ga<sup>3+</sup>, Fe<sup>3+</sup> or Mn<sup>3+</sup>; An<sup>-</sup> is a negatively charged layer between layers Anions, including CO<sub>3</sub><sup>2-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, etc.; x is the molar ratio of M<sup>3+</sup> to M<sup>2+</sup>+M<sup>3+</sup>, and z is the number of water molecules between layers<sup>[4-7]</sup>.

**Figure 1** is a schematic diagram of a typical Mg<sub>2</sub>Al-CO<sub>3</sub><sup>2-</sup>-LDH structure.



**Figure 1.** Crystal structure of Mg<sub>2</sub>Al-CO<sub>3</sub><sup>2-</sup>-LDH (Green balls = CO<sub>3</sub><sup>2-</sup>

Deep pink sticks = O of H<sub>2</sub>O or —OH, gray sticks = H of H<sub>2</sub>O or —OH, gray octahedra = Al, blue octahedra = Mg)

### 2.2 The nature of LDH

#### 2.2.1 Acidity and alkalinity

LDH has both acidic and basic characteristics. When the LDH layer contains a large amount of hydroxyl groups, the LDH is alkaline. The basic strength of LDH is basically determined by the basicity of the divalent metal hydroxide in the laminate. Due to the small specific surface area of LDH, its apparent alkalinity is weak. However, after the LDH is calcined, the specific surface area is increased, and the obtained product is more basic. Since the LDH laminate structure contains amphoteric trivalent metal oxides with a certain amount of anions between the layers, LDH also has weak acidity<sup>[8]</sup>.

#### 2.2.2 Regulatory

(1) The interlayer anions can be regulated: the anions located between the LDH layers can be intercalated by other inorganic anions, organic anions, complex anions, polymer anions, biochemical anions or heteropolyanions, i.e. interlayers of LDH Exchangeability of ions<sup>[9]</sup>. The ease of exchange of interlayer anions depends on the radius, spatial

structure and charge properties of the exchanged ions<sup>[10]</sup>.

(2) The composition of the laminate can be controlled: the valence and trivalent metal ions of the LDH laminate can be replaced by other metal ions with the same valence and similar radii, and the proportion of the elements can be adjusted by changing the ratio of the raw materials to make the charge of the laminate. Density and chemical properties change accordingly; metal ions can continue to be added to further form ternary or quaternary LDH-like compounds<sup>[11]</sup>.

(3) Crystal size and distribution can be controlled: The nucleation concentration and temperature of LDH can be controlled to control the nucleation rate of LDH. At the same time, the supersaturation, temperature and crystallization time of the crystal will affect the growth rate of LDH crystal. Therefore, LDH<sup>[12]</sup> with different crystal sizes and distributions can be obtained by controlling the synthesis conditions.

### 2.2.3 Thermal stability

LDH has good thermal stability. When the heating temperature is less than 200 °C, the desorption of water between the LDH layers is mainly dominant, while the structure change of LDH is small. When the heating temperature is 200 to 450 °C, CO<sub>2</sub> and H<sub>2</sub>O are released, and the hydroxyl group and carboxyl group of the LDH laminate are desorbed, and the specific surface area and pore volume of the material become large. When the heating temperature is higher than 450 °C, the lamellar structure of LDH collapses to form a double metal oxide (LDO), thereby increasing the specific surface area of the material, reducing the micropore volume, and improving the thermal stability<sup>[13]</sup>.

### 2.2.4 Structure memory effect

The structural memory effect refers to the phenomenon that LDO formed by thermal decomposition of LDH at 450-500 °C can be restored to an ordered layered structure of LDH under suitable conditions. The structural memory effect is related to the temperature at which LDH is decomposed. As the calcination temperature increases, the relative crystallinity decreases, which leads to a decrease in memory function. If the calcination temperature is too high, the decomposition products cannot be restored to the layered structure of LDH<sup>[14]</sup>.

Due to the special chemical and structural properties of LDH, LDH can be used as catalytic material<sup>[15]</sup>, water treatment adsorption material<sup>[16]</sup>, carbon dioxide adsorption material<sup>[17]</sup>, biosensing material<sup>[18]</sup>, drug sustained release material<sup>[19]</sup> and other applications.

Method for preparing 3LDH/polymer nano composite material

The introduction of LDH as a precursor into the polymer matrix, the synergistic action of LDH and polymer makes the composite material outstanding, and has shown excellent performance and great development potential in many fields<sup>[20,21]</sup>. The preparation methods of LDH/polymer nanocomposites mainly include blending method, intercalation compounding method, in-situ polymerization method, exfoliation/recombination method and reconstitution method, etc., and introducing LDH into water-soluble or water-insoluble polymers respectively. A composite material having different functions and different structures based on a polymer is obtained. A functional composite film mainly composed of LDH can also be obtained by a layer self-assembly method and a spin coating method.

## 3.1 blending method

### 3.1.1 Melt blending

Melt blending refers to mixing the polymer body with LDH under shear and high temperature conditions, and the polymer can enter the LDH layer or peel off to form a nanocomposite<sup>[22]</sup>. The melt blending method is suitable for the preparation of nanocomposites by mixing thermoplastic polymers with LDH<sup>[23]</sup>. The introduction of LDH can improve the thermal stability and crystallinity of the polymers. Xu Jianhua *et al*<sup>[24]</sup> prepared LDH/nylon 6 composites by melt blending nylon 6, LDH and halogen-free flame retardants. The results show that LDH and flame retardant can produce synergistic flame retardant effect on nylon 6, and can improve composite materials. Thermal stability.

In addition to nylon 6, the introduction of ZnAl-LDH into the ethylene-vinyl acetate resin can improve the thermal stability of the resin<sup>[25]</sup>; the addition of MgAl-LDH to the polypropylene (PP) resin accelerates PP crystallization and enhances it. Crystallinity<sup>[26]</sup>; Adding LDH to high density polyethylene (HDPE) gives fiber filaments with good mechanical properties<sup>[27]</sup>.

The melt blending method has the advantages of simple operation, environmental friendliness, and easy industrial production, but it is difficult to ensure uniform dispersion of the nanoparticles in the polymer system.

### 3.1.2 Solution blending

Solution blending refers to adding LDH or modified LDH to a polymer solution, and uniformly dispersing LDH or modified LDH in a polymer by mechanical stirring, ultrasonic or high-temperature heating to prepare a composite material. Wang *et al.*<sup>[28]</sup> first hydrophobically modified Zn<sub>2</sub>Al-boric acid-LDH and Mg<sub>3</sub>Al-boric acid-LDH by water-mixed solvent method<sup>[29,30]</sup>, making it easier to disperse in hydrophobic polymer. LDH and PP were subjected to high temperature reflow blending in xylene to obtain PP/LDH nanocomposites with excellent flame retardant properties. Nagendra *et al.*<sup>[31]</sup> separately prepared LDH gel and LDH dispersion and isotactic polypropylene (iPP) in xylene solution to prepare iPP/LDH composite (as shown in **Figure 2**). The results showed that a small amount of LDH could be added. Improve the thermal stability, nucleation performance and crystallization properties of iPP. In addition to iPP, LDH also has a significant effect on PP nucleation, crystallization and other properties<sup>[32]</sup>. Compared to melt blending, this process can increase the dispersion of LDH in the polymer system, but it can cause solvent contamination.



Fig.2 Schematic illustration of iPP/LDH nanocomposite by MgAl-LDH gel and sonicated LDH via solution blending<sup>[31]</sup>

### 3.2 Intercalation composite method

The intercalation composite method refers to directly intercalating a polymer into an LDH sheet layer to form a nanocomposite material having an intercalation or exfoliation structure. Usually, the LDH needs to be pre-intercalated to increase the layer spacing to facilitate subsequent intercalation recombination. According to the state of the polymer, it can be divided into three methods: solution intercalation, melt intercalation and emulsion intercalation.

The solution intercalation method generally disperses LDH into a polymer solution, and the polymer molecular chain can ion exchange with the anion between the LDH layers under certain conditions, so that the polymer molecular chain enters between the LDH layers. Qu *et al.*<sup>[33]</sup> modified ZnAl-LDH with sodium dodecyl sulfate (SDS) and dispersed ZnAl-LDH (SDS) into xylene solution containing linear low density polyethylene (LLDPE). The results showed that LDH The introduction can improve the thermal stability and mechanical properties of LLDPE. The DS-modified LDH is dispersed into a polyvinyl chloride (PVC) tetrahydrofuran solution<sup>[34]</sup> or a polyethylene oxide (PEO) aqueous solution<sup>[35]</sup> by the same method, and can be obtained in different dispersed phases. High thermal performance composites. However, solution intercalation requires the selection of a suitable solvent to dissolve the polymer. If the solvent is organic, it is likely to cause environmental pollution and increase production costs.

Melt intercalation recombination means that the thermoplastic polymer is intercalated directly into the LDH layer under the action of shear force by the thermoplastic polymer. Du *et al.*<sup>[36]</sup> firstly used SDS and nitrate ion pre-intercalation to enter the MgAl-LDH layer, and the modified LDH and LLDPE were intercalated by melt

intercalation. The results show that the LDH is pre-modified and the interlayer spacing is increased. A nanocomposite having a peeling structure, and the addition of LDH can improve the thermal stability of LLDPE. In addition, nylon 6<sup>[37]</sup> and PP<sup>[38]</sup> can also be intercalated into the modified LDH layer in a molten state to prepare a thermally stable composite. Melt intercalation is simple and easy, but it consumes a lot of energy.

Emulsion intercalation refers to the insertion of polymer latex particles into the LDH layer under mechanical shear to form a nanocomposite. Shouldice *et al*<sup>[39]</sup> modified LDH with terephthalate, and then prepared LDH/polystyrene emulsion by emulsion intercalation method. It was found that when the emulsion concentration reached 1/5 of the LDH anion exchange capacity, LDH The sheet will peel off and form a state similar to complete peeling; when the emulsion concentration is high, an emulsion intercalated LDHs composite will be formed. The emulsion intercalation operation is simple and convenient, and is environmentally friendly, and the obtained composite material can be directly applied, and has certain advantages.

### 3.3 In-situ polymerization

#### 3.3.1 In situ polymer formation

In-situ polymer formation means that the modified or unmodified LDH is thoroughly mixed with the polymerizable monomer, and the monomer is introduced into the LDH layer by coprecipitation or ion exchange, and then induced by heating, illumination or addition. The manner of the agent initiates polymerization of the monomer between the LDH layers to prepare an LDH/polymer nanocomposite. Wang *et al*<sup>[40]</sup> first intercalated acrylate monomer to LDH, and then initiated free radical polymerization by stepwise addition of initiator AIBN to prepare polymethyl methacrylate (PMMA)/LDH nanometer with exfoliation structure. Composite material.

In addition to free radical polymerization, LDH/nylon 6 composites can be prepared by initiating polycondensation of caprolactam between LDH layers<sup>[41]</sup>; intercalating diisocyanate monomers into LDH layers, and then adding polyethylene glycol and chain extender Polyurethane/LDH nanocomposites can be prepared by addition polymerization with a catalyst<sup>[42]</sup>.

#### 3.3.2 Generate LDH in situ

The in-situ LDH method is to prepare an LDH/polymer nanocomposite by mixing a polymer with a metal salt capable of forming LDH and in situ forming an LDH sheet under certain conditions. The molecular weight and concentration of the polymer are key factors influencing the preparation of the composite. Wilson *et al*<sup>[43]</sup> mixed anionic polymer polystyrene-4-sulfonic acid (PSS) or sodium polystyrene sulfonate (PSSNa) with Mg(NO<sub>3</sub>)<sub>2</sub> and Al(NO<sub>3</sub>)<sub>3</sub> solutions under alkaline conditions. The composite material with polymer intercalated LDH was obtained. The results show that the molecular weight of the polymer has a certain influence on the nucleation and growth of LDH.

In order to investigate the influence of molecular weight of polymer on the nucleation growth of LDH, a method for preparing LDH intercalation materials on a large scale was explored. Yu *et al*<sup>[44]</sup> mixed Mg(NO<sub>3</sub>)<sub>2</sub> and Al(NO<sub>3</sub>)<sub>3</sub> metal salt solution. The PSSNa/LDH intercalation composites were obtained by mixing with PSSNa. The results show that the higher the concentration of PSSNa, the better the formation of composites. When the molecular weight of PSSNa increases, the nucleation performance of LDH decreases.

#### 3.3.3 double in situ polymerization

The double in-situ polymerization method refers to mixing a polymerizable monomer with a metal salt raw material solution capable of forming LDH, and forming a LDH by metal ion precipitation, and a polymer or a monomer enters between the LDH layers, and the initiator continuously initiates polymerization of the monomer to form an LDH. / Polymer nanocomposites. Chen *et al*<sup>[45]</sup> added Mg(NO<sub>3</sub>)<sub>2</sub>, Al(NO<sub>3</sub>)<sub>3</sub>, methyl methacrylate (MMA), benzoyl peroxide (BPO), SDS, and then added sodium hydroxide, followed by thermal initiation polymerization. The PMMA/LDH nanocomposite was prepared by bulk copolymerization.

The preparation of composites by intercalation recombination requires sufficient thermal power to intercalate the polymer chains into the LDH layers. Compared with the intercalation composite method, the in-situ polymerization method has lower requirements on thermodynamics, but has higher requirements on the matching of polymer and LDH

laminate. In-situ polymerization can achieve better dispersion of LDH in the polymer.

### 3.4 stripping / recombination method

The stripping/recombination method is also called delamination/adsorption method. Firstly, LDH is pre-stripped in a solution, and then a polymer or a polymerizable monomer is added, and after blending or polymerizing, an LDH/polymer nanocomposite is obtained. Due to the high charge density of the LDH laminate, direct delamination of the LDH in the solution system requires a strong mechanical action and requires the selection of a suitable solvent. Li *et al*<sup>[46]</sup> first prepared a LDH stripped colloidal solution in a formamide solution, and then blended the colloidal solution with polymethyl methacrylate (PMMA) in an acetone solution to obtain a rapid evaporation of the organic solvent. PMMA/LDH nanocomposites with good thermal stability.

In addition to the mechanical action of the LDH in the solvent, the stepwise chemical modification of the stripped LDH can also be employed. Yuan *et al*<sup>[47]</sup> first obtained the LDH of DS intercalation, then introduced the epoxy group by KH560 modified LDH; and then used trimethylolpropane trimethyl decylacetate (TMPT) and modified epoxy on LDH. The group reacted to prepare a thiol-terminated modified LDH (LDH-SH) having a peeling structure, and LDH-SH and an acrylic resin were composited by ultraviolet curing to prepare an LDH/polymer nanocomposite having a peeling structure.

The stripping/recombination method can be used not only for the synthesis of LDH/polymer nanocomposites, but also for the preparation of highly ordered nanocomposites in combination with layer assembly, electrostatic deposition or additional shear force fields.

### 3.5 reconstruction method

The reconstruction method is a composite material preparation method based on the "structure memory effect" of LDH. The LDO is mixed with an anionic polymer or a polymerizable monomer solution. Under certain conditions, the LDH partial lamel structure is restored. During the reconstitution process, polymer chains or polymerizable monomers enter the LDH layer to form or initiate polymerization to form LDH/polymer nanocomposites<sup>[48]</sup>. Letoux *et al*<sup>[49]</sup> mixed LDO with PSS aqueous solution and successfully prepared PSS/LDH intercalated nanocomposites by structural memory effect reconstruction. The morphology and crystallization properties were similar to those of direct intercalation products.

### 3.6 layer self-assembly method

Layer-by-layer (LbL) assembly is a method for preparing LDH nanosheet/polymer composite film by electrostatic assembly with anionic polymer by using the positive charge of LDH nanosheet. The cleaned substrates were immersed in the LDH sheet dispersion and the polymer solution, respectively, and assembled in multiple times to obtain an LDH/polymer nanocomposite film. Liu *et al*<sup>[51]</sup> first stripped CoAl-LDH nanosheets in formamide, and repeatedly immersed the clean substrate in LDH colloidal dispersion and PSS aqueous solution to obtain PSS/CoAl-LDH multilayer ultrathin film.

In addition to PSS, anionic polymer sulfonated p-methylenebenzene derivatives (APPP)<sup>[52]</sup> and polyparaphenylene vinylene<sup>[53]</sup> can be assembled with exfoliated LDH sheets to prepare composite films. In addition to the common binary assembly, the exfoliated LDH nanosheets and graphene oxide sheets are simultaneously combined with polyvinyl alcohol (PVA) by LbL to obtain films with excellent electrical conductivity<sup>[54]</sup>. Existing literature reports indicate that the method for preparing composite films by LbL has wide applicability. In principle, negatively charged polymers can be assembled with exfoliated LDH nanosheets, and the obtained functional films also have many potential applications.

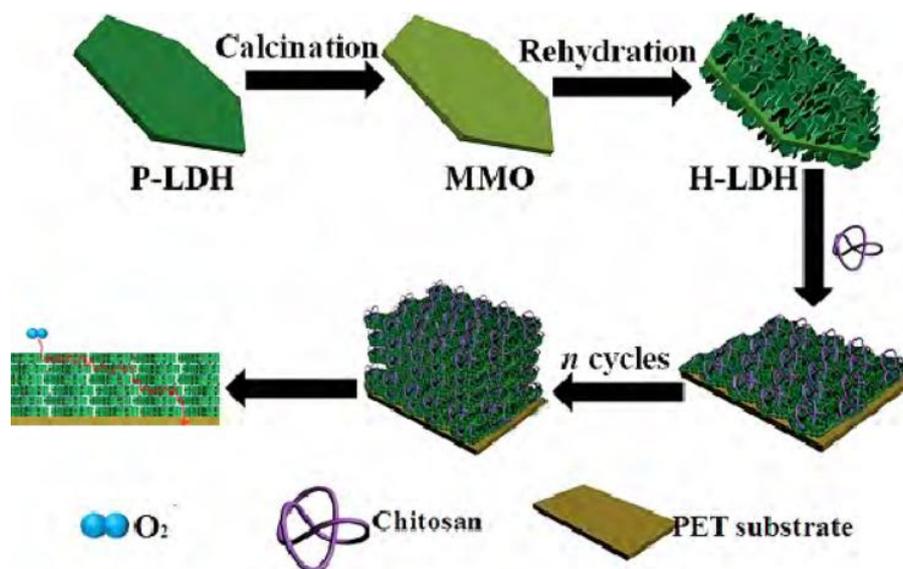


Figure 3. Schematic representation for the fabrication of (P-LDH/CTS) $_n$  films<sup>[56]</sup>

### 3.7 spin coating

The spin coating method is a method of preparing a film on a smooth substrate, and the polymer previously placed on the substrate is uniformly distributed by high-speed rotation to obtain a film having a uniform thickness<sup>[55]</sup>. Preparation of LDH/polymer nanocomposites by spin coating requires preparation of LDH colloidal solution, followed by mixing or alternately injecting the colloidal solution with the polymer and rotating to obtain a composite film. Pan *et al.*<sup>[56]</sup> obtained a multi-stage LDH (H-LDH) suspension by roasting recovery method, and adsorbed the pre-cleaned polyethylene terephthalate film on a spin coater, and then H- The (L-LDH/CTS) $_n$  composite film was obtained by alternately spin-coating LDH suspension with polymer chitosan (CTS). The film has excellent oxygen barrier properties (as shown in **Figure 3**). They<sup>[57]</sup> also obtained an LDH/rubber multilayer composite film with excellent gas barrier properties by the same method.

The composite film is prepared by the spin coating method, and the advantages thereof are that the film thickness is precise and controllable, energy saving, high cost performance, low pollution, etc., and the technology can also play an important role in the research and development of microelectronics and biological materials.

## 4. Application of 4LDH/polymer nanocomposites

Due to the excellent structure of LDH, high ion exchange capacity and good thermal stability, the composite of polymer and nano-composite will have different functional properties, in flame retardant, UV/IR absorption, medical, Wide range of applications in water treatment, gas barrier, luminescence and energy storage.

### 4.1 Flame retardant materials

Magnesium hydroxide and aluminum hydroxide can reduce the surface temperature of the material due to the endothermic reaction during combustion, and are often used as an inorganic filler to improve the flame retardancy of the material<sup>[58]</sup>. LDH has similar structure and composition to aluminum hydroxide and magnesium hydroxide. It has the advantages of both, and it does not contain toxic and harmful substances. It is an ideal flame retardant and smoke suppressant material<sup>[59, 60]</sup>.

Adding LDH as a filler to the polymer can significantly improve the flame retardant properties of the material. Nyambo *et al.*<sup>[25]</sup> prepared MgAl-LDH and ZnAl-LDH by coprecipitation method, and then blended with ethylene-vinyl acetate copolymer (EVA) by melt blending. The results showed that the addition of LDH could improve EVA. Thermal stability and flame retardant properties; LDH dosage of 3% can reduce the peak heat release rate of EVA by 40%, and the flame retardant performance is significantly better than magnesium hydroxide or aluminum hydroxide. In addition

to EVA, LDH can also be used for flame retardancy of polymers such as PMMA<sup>[61]</sup>, polyester resin (UP)<sup>[62]</sup>, PVA<sup>[63]</sup>, PVC<sup>[64]</sup>.

LDH can also be combined with other inorganic particles to synergistically exert a flame retardant effect on the polymer. Wang *et al*[65] used the positive charge of LDH sheet and the negatively charged  $\beta$ -FeOOH to assemble the LDH  $\beta$ -FeOOH rod, and then LDH- $\beta$ -FeOOH and epoxy resin (EP) were compounded by melt blending. The uniform distribution of LDH on  $\beta$ -FeOOH is beneficial to improve the flame retardancy of composites.

## 4.2 UV / infrared absorption materials

MgAl-CO<sub>3</sub>--LDH has a certain infrared absorption at 1428~1250cm<sup>-1</sup> due to the presence of carbonate, so it can be added as a filler to PE to obtain a film material with thermal insulation properties<sup>[66,67]</sup>. Since MgAl-CO<sub>3</sub>--LDH has no infrared absorption at 1100-1200 cm<sup>-1</sup>, in order to further improve the absorption efficiency of LDH, the exchangeability of anions between LDH layers can be utilized to intercalate the infrared absorbing material into the LDH layer and then The polymer is compounded to obtain a highly efficient infrared absorbing material. Iminodiacetic acid (IDA) contains CN, N-H and COOH groups and has strong infrared absorption properties at 1800-900 cm<sup>-1</sup>. Wang *et al*[68] intercalated IDA into the LDH layer to obtain MgAl-IDA-LDH, and blended it with low density polyethylene (LDPE) to prepare a composite film with excellent infrared absorption properties to improve the thermal insulation properties of the film material. Aminotrimethylene phosphonic acid[69] can also be intercalated between the LDH layers to obtain an agricultural film material excellent in thermal insulation properties.

Similarly, the ultraviolet absorber can also be intercalated between the LDH layers to obtain a composite material having ultraviolet absorption properties. 4,4-Diaminopurine-2,2-disulfonate (DASDSA) is an excellent UV absorber. Gao *et al*[70] first used DASDSA to intercalate LDH and then use solution blending. The composites with UV absorption properties were prepared by compounding with PP. The results show that the introduction of DASDSA-LDH in PP can significantly improve the UV absorption of the composites in the wavelength range of 200-600 nm.

## 4.3 medical materials

LDH has low toxicity and good biocompatibility, which has broad application prospects in the biological field<sup>[71,72]</sup>. Due to the exchangeability of the interlayer anions of LDH, anionic drug molecules can be intercalated into the LDH layer to form an effective package, and the controlled release of the drug can be achieved under physiological conditions of pH 7-8. Xu *et al*<sup>[73]</sup> inserted the ophthalmic drug into the LDH layer to obtain the drug-loaded composite LDH-drug, and then prepared the polyhydroxyethyl methacrylate (PHEMA) hydrogel-LDH-drug complex by in-situ polymerization. Membrane, the sustained release rate of the drug-loaded film within a few days is 50% to 70%. Mahkam *et al*<sup>[74]</sup> prepared LDH-polymer nanocomposites with effective drug sustained release properties by interfacial crosslinking by using LDH, pH-responsive polymer, and alginate encapsulated insulin. Since the LDH laminate is positively charged, it can be used for the preparation of the gene vector by utilizing the electropositive and biomolecule effects of the laminate. Hu *et al*.<sup>[75]</sup> used the hydroxyl group on the surface of LDH to attach the initiation point of the ATRP reaction containing a disulfide bond to the surface, and then initiated the polymerization grafting of N,N-dimethylaminoethyl methacrylate on the surface of LDH. The ester (PDMAEMA) obtained a series of gene carriers having a layered LDH as a matrix and a cationic polymer as a side chain. The results showed that the gene carrier with the flaky LDH matrix had better intracellular conversion and transfection efficiency.

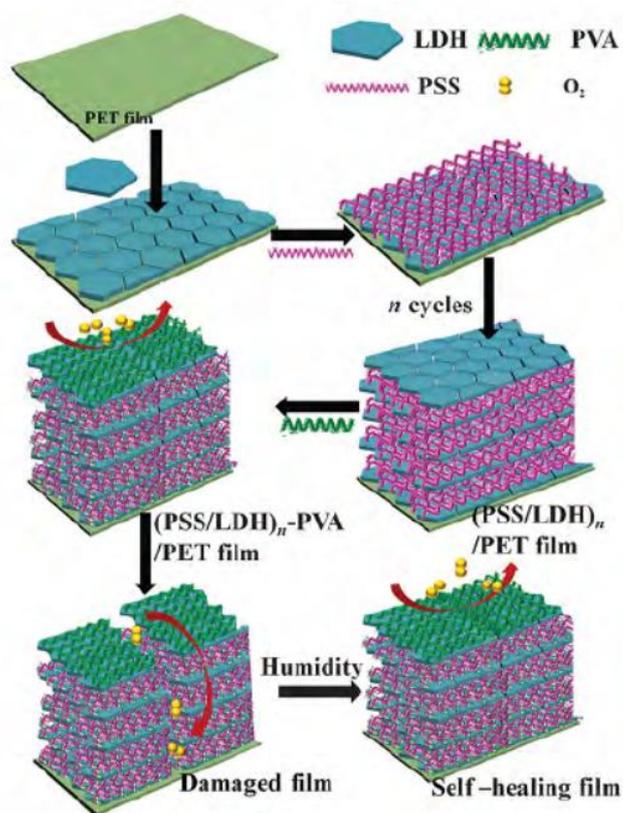
## 4.4 Water treatment

Materials researchers usually use LDH's high specific surface area and strong interlayer anion exchange capacity to apply its ion exchange product or its calcined product LDO in water treatment. Hibino[76] first prepared LDH of lactic acid intercalation layer, and then blended it with uncharged agarose polymer at high temperature to obtain LDH/agarose complex gel. The application results showed that when the ratio of LDH to agarose reached 1 At 1 o'clock, the composite gel has good adsorption properties for SO<sub>4</sub><sup>2-</sup>, I<sup>-</sup>, and HPO<sub>4</sub><sup>2-</sup>.

In addition to the combination of LDH and polymer for adsorption, LDO is also widely studied for water treatment adsorption<sup>[77,78]</sup>, and the application of LDH in water treatment can also be reflected in the field of photocatalysis<sup>[79,80]</sup>.

#### 4.5 gas barrier material

Dispersing the highly oriented inorganic layer filler into the polymer can prolong the diffusion path of the gas molecules, inhibit the diffusion of gas molecules, and thereby improve the gas barrier properties of the film. LDH has a multi-layered structure and a large aspect ratio. It is often used in the packaging of foods and pharmaceuticals to prevent the penetration of gases such as oxygen and the deterioration of foods and medicines. Dou *et al*[81] prepared a composite membrane by pre-stripping MgAl-LDH and PSSNa through layer-by-layer self-assembly method, and combined it with PVA to obtain a film with excellent gas barrier properties (as shown in **Figure 4**), and because of PVA Hydrogen bonding can be formed between the hydroxyl group and water, so that the film has a self-repairing function under wet conditions. After<sup>[82]</sup>, the LDH/polyacrylic acid (PAA) composite film was also obtained by layer-by-layer assembly method, and the void-filled with CO<sub>2</sub> was used to prepare a composite material (LDH/PAA) n-CO<sub>2</sub> with brick-gray-sand structure, of which LDH As a brick, PAA is used as ash, and CO<sub>2</sub> acts as a sand to fill the gap, and the obtained composite material has excellent gas barrier properties.

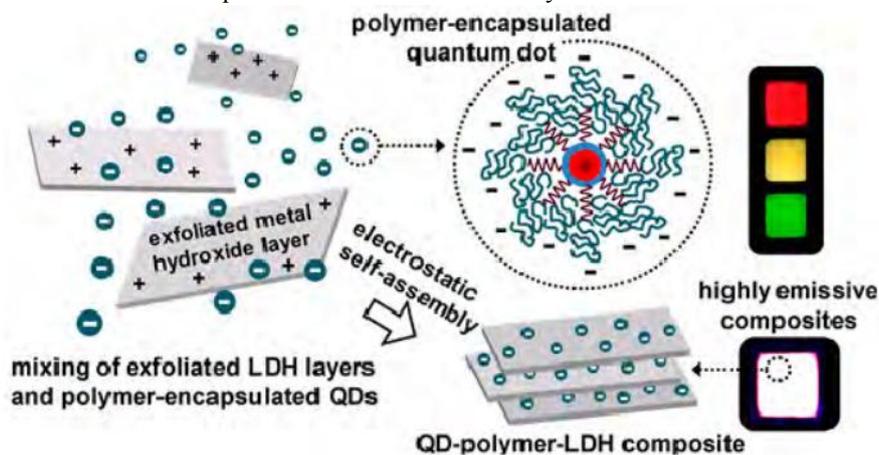


**Figure 4** Schematic illustration of the fabrication of (PSS/LDH)-OVA film serving as a oxygen barrier film with self-healing ability<sup>[80]</sup>

#### 4.6 luminescent materials

Quantum dots have quantum confinement effects and are widely used in the preparation of nanophotovoltaic materials. However, quantum dot luminescence is susceptible to external environment, aggregation effects, etc., and thus its quantum yield and luminous efficiency are easily reduced. LDH has a dispersing and fixing effect on the fluorescent molecules, which can effectively avoid the agglomeration of the fluorescent molecules, thereby improving the luminous efficiency. Cho *et al*<sup>[83]</sup> wrapped quantum dots (QD) into the hydrophobic cavity of the polymer and used electrostatic interaction with the pre-stripped ZnAl-LDH colloid solution to obtain QD-polymer/LDH composite (as

shown in **Figure 5**). The dual protection of QD by polymer and LDH makes the light stability of QD significantly enhanced, and still has good light intensity after 80 hours of illumination. Qin *et al.*<sup>[84]</sup> mixed the neutral polymer poly-N-vinylcarbazole (PVK) and the phosphorescent molecule Ir(F2ppy)<sub>3</sub>, and obtained the Ir(F2ppy)<sub>3</sub>@PVK/LDH composite membrane by layer-by-layer self-assembly method; The rigid structure of LDH nanosheets can fix and separate luminescent molecules and improve their luminous efficiency.



**Figure 5.** Schematic illustration of the self-assembly process for the formation of QD-polymer-LDH composites with good fluorescence intensity<sup>[83]</sup>

## 4.7 energy storage materials

LDH has the advantages of high electrochemical activity, good stability and low price. Therefore, LDH-based electrode materials have been widely used in electrochemical sensors, fuel cells and supercapacitors<sup>[85, 86]</sup>. Zhao *et al.*<sup>[87]</sup> used self-assembly method to combine CoNi-LDH with conductive polymer poly(3,4-ethylenedioxythiophene): polystyrenesulfonic acid (PEDOT:PSS) to obtain supercrystals, LDH and homogeneous conduction. The layer interface is closely connected to enhance the transport of ions and charge carriers, and also to improve the specific heat capacity and charge and discharge performance of the capacitor. In addition, Han *et al.*<sup>[88]</sup> grown a CoNi-LDH core-shell nano-array coated with poly(3,4-ethylenedioxythiophene) on a flexible nickel foil substrate to obtain a capacitor with excellent electrochemical performance.

Song *et al.*<sup>[89]</sup> first prepared a functionalized graphene sheet (FEG) with a partially exfoliated structure, thereby depositing NiCo-LDH as the cathode/polypyrrole (PPy) as the anode electrode material with FEG as the substrate; The two electrode materials are assembled to obtain a high speed asymmetric capacitor (ASC). The ASC has good cycle stability and can achieve 91% capacitance retention after 5000 cycles of charge and discharge.

## 5. Conclusion

As a clay material with unique structure and excellent performance, LDH has been added to polymers as a nano-filler in various ways, which has attracted the attention of scholars in many fields. Composite materials have been widely used in flame retardant, gas barrier, heat preservation, sustained release, adsorption, photoelectric and other fields. The author believes that LDH/polymer nanocomposites will further develop in the following directions.

Although the composites of intercalated or exfoliated structures can be obtained in the reported methods, there are few studies on the influence of different structures on the properties of composites. Therefore, the research on the relationship between structure and properties of LDH/polymer nanocomposites still needs to be further strengthened, which is helpful to guide the choice of structural design and synthesis methods of composite materials.

At present, the research of LDH/polymer nanocomposites is no longer limited to the combination of a single LDH and a polymer. There have been a few studies on the use of LDH together with other inorganic particles to improve the performance of certain materials, such as LDH and  $\beta$ -FeOOH. Synergistically used for polymer flame retardant<sup>[64]</sup> and

so on. Binary or multi-component inorganic materials are combined with polymers. On the one hand, LDH and other inorganic particles play a synergistic role to meet the performance requirements of the material, and on the other hand, the versatility of the composite material can be achieved.

The field of application of LDH/polymer nanocomposites can be further expanded. Due to the lamellar structure and positive electrical properties of LDH, it is added to the light-spinning polymer matrix, which is expected to improve the combination of light-spinning aids to anionic materials such as dyes. It is used in the preparation of emulsions such as oil plugging agents. It can replace the surfactant to stabilize the latex particles, and obtain a positively charged emulsion to help improve the affinity of the blocking agent to the rock.

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