

Synthesis and Application of Magnetic Fe₃O₄/Layered Double Hydroxide Nanoparticles

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Summary: During the past decade, significant progress has been made in synthesizing various nano-based products for industrial application. Among them, magnetic Fe₃O₄/layered double hydroxides nanocomposite materials have attracted broader applicability. The uniqueness of these nano hybrid nanocomposites have attracted valuable utility to nanotechnology field due to their magnetic properties and enhanced catalytic performance compared to layered double hydroxides (LDHs). The electrostatic interaction between positively charged LDHs and negatively charged Fe₃O₄ makes them more stable. Therefore, the present review article summarizes the various synthesis strategies and applications of magnetic Fe₃O₄/LDHs.

Keywords Fe₃O₄, LDHs, Nanocomposite, Nanotechnology, Electrostatic interaction

Introduction

The structure of layered double hydroxides (LDHs) is represented by the general formula $[M_1^{2+} M_x^{3+}(\text{OH})_2]^{x+} \cdot [A_{x/n}]^{n-} \cdot m\text{H}_2\text{O}$, where M^{2+} and M^{3+} are the divalent and trivalent metal ions, respectively. A^{n-} denotes the interlayer anions that balance the positive charges on the layers, and x is defined as the molar ratio of M^{2+} to $(M^{2+} + M^{3+})$. Therefore, LDHs are positively charged substances, which is caused by the isomorphous replacement of M^{III+} to M^{II+} in the LDHs sheet layer [1, 2]. Their unique characteristics makes them suitable for use as: photocatalysts, solid base catalysts [3], LDH-drug hybrids adsorbents [4, 5], among others (Fig1). Studies have revealed that single application of LDHs as a catalyst is limited. For example, it is difficult to separate and recover LDHs from the reaction system after catalysis or adsorption [6]. Studies have shown that there are 32 O_2^- closely packed face-centered cubic lattices in the unit cell of Fe₃O₄. Fe²⁺/Fe³⁺ occupies the octahedral and tetrahedral voids, respectively. Adjacent Fe²⁺ or Fe³⁺ exchanges electrons through O_2^- in the middle, and neighboring electrons jump back and forth between the transfers of O_2^- . This special structure makes Fe₃O₄ have good conductivity and strong magnetism [7].

It has been revealed that LDHs and Fe₃O₄ have positively and negatively charged surfaces, respectively, and the two can be combined through electrostatic interaction. This theory provides theoretical support for the assembly of Fe₃O₄/LDHs.

Multiple experimental results show that the introduction of magnetic substances into LDHs not only retains the performance of LDHs itself, but also obtains magnetic catalysts, adsorbents and magnetic targeting agents with magnetic responsiveness [8]. However, the composite material will have a lower specific saturation magnetization. This is due to the fact that Fe₃O₄ undergoes partial crystal phase transformation during the firing process, and it may also be affected by LDHs. In general, the composite Fe₃O₄/LDHs are designed to meet the following requirements: (i) Posses the properties of both Fe₃O₄ and LDHs at the same time, (ii) convenient in recycling, (iii) contain certain degree of reusability. Therefore, this article reviews the preparation methods and applications of magnetic Fe₃O₄/LDHs nanocomposites.

Preparation method of Fe₃O₄/LDHs

Different preparation methods can obtain different crystal structures of the same substance, thereby affecting its performance and use. According to literature, Fe₃O₄/LDHs preparation methods mainly include: co-precipitation method, hydrothermal method, in-situ growth method, ion exchange method and thermal decomposition-reconstruction method (Table 1). In this section, we briefly discuss various key preparation methods of Fe₃O₄/LDHs nanoparticles.

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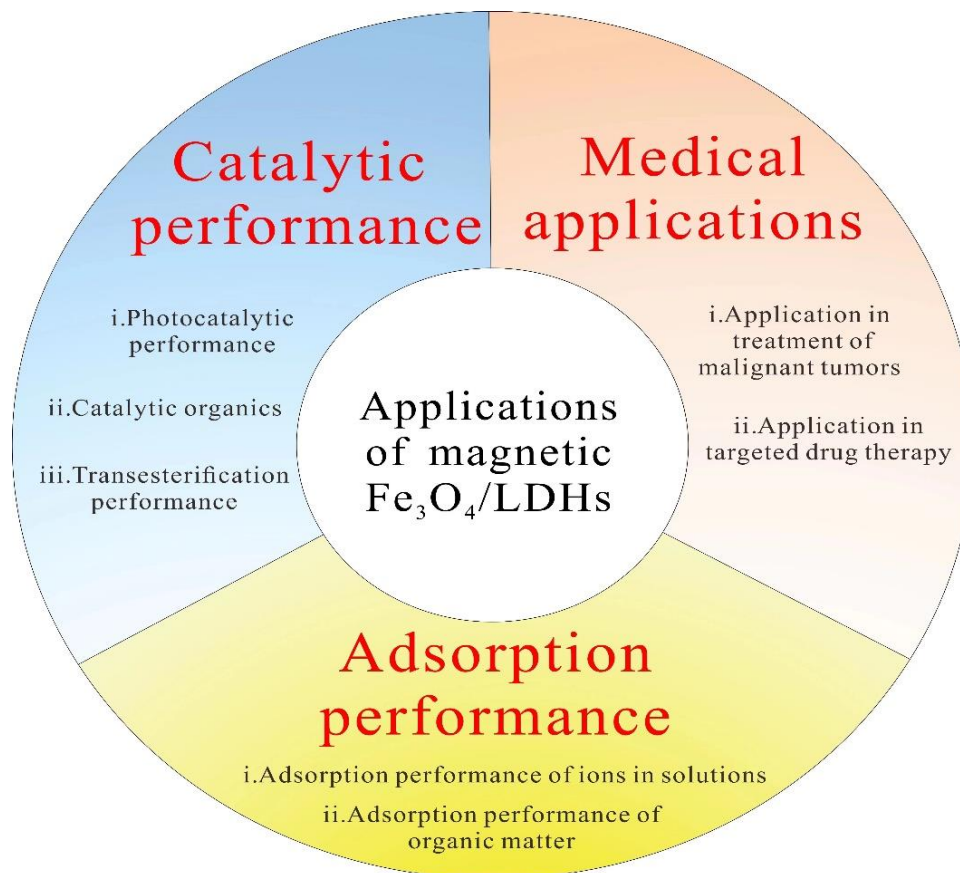


Fig 1. Application of magnetic $\text{Fe}_3\text{O}_4/\text{LDHs}$ nanoparticles.

Co-precipitation method

The co-precipitation technique involves the addition of M^{2+} and M^{3+} drop wise together and with the solution of the anion to be intercalated, under continuous stirring in the reactor. The pH is kept at constant during the reaction. The presence of hydroxide (alkaline solution) makes M^{2+} and M^{3+} nucleate and grow on the surface of Fe_3O_4 . Therefore, it is easier to obtain $\text{Fe}_3\text{O}_4/\text{LDHs}$ with relatively pure crystal form. During the preparation process, the use of different types and concentrations of M^{2+} , M^{3+} , alkali and pH will all have a certain effect on the properties of the synthesized material. At the same time, certain protective measures must be taken when crystals with a narrow particle size distribution are prepared through co-precipitation. When obtaining $\text{Fe}_3\text{O}_4/\text{LDO}$ by roasting, it is necessary to add certain protective measures such as nitrogen protection to prevent crystal phase transformation of Fe_3O_4 and other crystals added Fe_3O_4 in 150 mL of distilled water for ultrasonic dispersion for 15 minutes, and then placed it in a 60°C water bath and stirred vigorously [6, 9]. Using NaOH and Na_2CO_3 as precipitating agents to maintain the pH at around 10,

$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were precipitated to produce $\text{Fe}_3\text{O}_4/\text{MgAl-LDHs}$. In addition, Koilraj *et al* used the co-precipitation method to synthesize nitrate-intercalation by using Fe_3O_4 suspension and metal nitrate with a Mg/Al molar ratio of 2 as the raw materials, 2mol NaOH and 0.02 mol NaNO_3 as precipitating agents to synthesize $\text{Fe}_3\text{O}_4/\text{Mg}_2\text{Al-LDHs}$ [10]. The complete synthesis procedure was carried out in a nitrogen atmosphere to eliminate CO_2 pollution. Furthermore, Jung *et al* used the same method to add the Mg/Al mixed media into the Fe_3O_4 suspension, and prepared Fe_3O_4 with a mixed solution of 1M NaOH and 0.5M NaHCO_3 under the condition of pH=10 and prepared $\text{Fe}_3\text{O}_4/\text{MgAl-LDHs}$ composite materials with varying Mg/Al molar ratios (4:1, 3:1 and 2:1) (the preparation process is detailed in Fig 2) [11]. Increase of the Mg/Al molar ratio, resulted in increased interlayer spacing and specific surface area of the plates, which has an important impact on the adsorption performance of the adsorbent. The Mg/Al ratio of 4:1 has a large specific surface area, a large interlayer spacing, and an adsorption capacity of nearly 105.04mg/g, which is more suitable for the adsorption of large anions

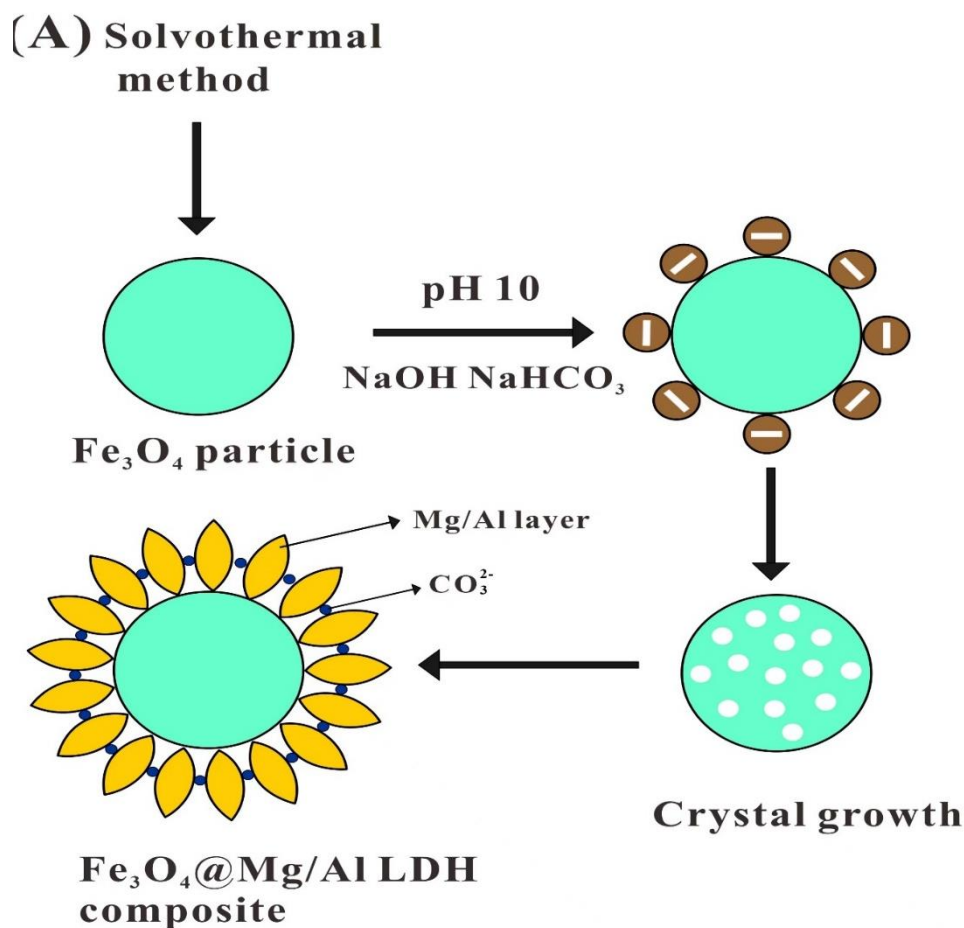


Fig. 2: Schematic diagram of synthesis of Fe₃O₄/Mg/Al LDH composites using co-precipitation method [11].

Water is a commonly used dispersant in co-precipitation. Studies have shown that in an impure water system, using a mixture of organic matter and water as a dispersant is also an essential method for making Fe₃O₄/LDHs. Under the combined action of proper particle concentration and solvent effect, metal ions rapidly adsorb on negatively charged Fe₃O₄ surface effectively inducing LDHs microcrystals to nucleate on the Fe₃O₄ surface and grow slowly and vertically. Zhao *et al* used water and methanol-water as dispersants to disperse Fe₃O₄, and prepared Fe₃O₄@CuNiAl-LDHs magnetic core-shell composites by co-precipitation. The results showed that in methanol-water and water media, CuNiAl-LDHs co-precipitated on the surface of the hollow Fe₃O₄ sub-microspheres, with strong magnetization, particularly the composite material obtained in water media was honeycomb-shaped, staggered on the Fe₃O₄ surface [12]. Similarly, Zhang *et al* used the same method to prepare Fe₃O₄@CuMgAl-LDHs by dispersing Fe₃O₄ into methanol solutions of different concentrations[13]. The vibrating sample

magnetometer results demonstrated that all samples displayed superparamagnetism. The magnetic saturations of Fe₃O₄@CuMgAl-2 and Fe₃O₄@CuMgAl-1 reduced to 60.5 and 51.0emu·g⁻¹, respectively, while Fe₃O₄ was 74.2 emu·g⁻¹

Co-precipitation method involves adding the metal solution and the precipitant dropwise to the reaction system under stirring conditions for reaction. Therefore, the preparation method is relatively simple, and the production cost is low. However, the co-precipitation reaction proceeds immediately when the materials are in contact. The instantaneousness of the reaction is strong, and the product is easy to agglomerate. Thus, it is necessary to strictly regulate the molar ratio between the reactant ions, pH, stirring speed, dropping speed and other factors and this makes the microscopic morphology of synthetic particles not easy to control.

Hydrothermal synthesis method

Another important synthesis technique is the hydrothermal synthesis method. This method is

different from the co-precipitation method in the sense that hydrothermal synthesis method uses soluble M^{2+} and M^{3+} solutions as raw materials, disperses the synthesized Fe_3O_4 ultrasonically, and adds a certain amount of alkali, usually NaOH, urea, ammonia, among others, mixed evenly and then added to the hydrothermal kettle, placed at a certain temperature and pressure for reaction. This method can better prevent the volatilization of the solution and is beneficial to the nucleation reaction. The experiment can optimize the structure and the size of the produced Fe_3O_4 /LDHs by changing parameters like pH, pressure, temperature and feeding ratio of the hydrothermal treatment [11]. The hydrothermal technique is among the most effective methods for making materials with diverse morphologies. In this process, water is added in hydrothermal kettle and the reaction is conducted under high temperature and pressurized conditions. If a non-aqueous or water-organic mixed solution is used as a medium for chemical reactions, it is also an effective means for assembling Fe_3O_4 /LDHs.

Chen *et al* dispersed 0.2 g of Fe_3O_4 into $Cr(NO_3)_3 \cdot 9H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ solutions and adjusted the pH with $NH_3 \cdot H_2O$ [14]. With the aid of microwave, Fe_3O_4 /ZnCr-LDHs with hexagonal morphology, particle size close to 50-150 nm and surface area of 114 m^2/g were synthesized via hydrothermal method. After the reaction, the separation from the system was completed under the action of an external magnetic field. In addition, Hou *et al* mixed 40 mL of ethylene glycol and 2.0 g of $FeCl_3 \cdot 6H_2O$ and after the mixture was uniformly mixed [15], 20 mL of ethylenediamine, 6.0 g of $CH_3COONa \cdot 3H_2O$ and 0.8 g of MgAl-LDHs powder were gradually transferred to the above media. After stirring for 30 minutes, the mixture was transferred to a hydrothermal kettle, heated to 200 °C, and kept for 8 hours to prepare Fe_3O_4 /MgAl-LDHs, followed by

calcination at 500 °C to obtain Fe_3O_4 /MgAl-LDO. The results showed that Fe_3O_4 /MgAl-LDHs had the characteristic structure of lamellar platelets. The presence of uneven dark spots (Fe_3O_4) indicated that the prepared material was a composite of MgAl-LDHs and Fe_3O_4 . After calcination, compared with Fe_3O_4 /MgAl-LDHs, Fe_3O_4 /MgAl-LDO had a smaller size and smooth edges. The lattice spacing of Fe_3O_4 /MgAl-LDHs and Fe_3O_4 /MgAl-LDO were 0.206nm and 0.252nm, respectively. Infrared showed that Fe_3O_4 /MgAl-LDHs had a large number of hydroxyl vibration peaks, and the hydroxyl vibration peaks of Fe_3O_4 /MgAl-LDO almost disappeared. The saturation magnetization was 13.06 emu/g and 11.85emu/g, which were enough to separate them from the system quickly under the action of an external magnetic field. The hydrothermal method is conducive to the nucleation reaction and can prepare Fe_3O_4 /LDHs with better dispensability. However, this method needs to be carried out under high temperature and high pressure, which requires many equipment, and therefore the cost is relatively high.

In situ growth method

The in-situ growth method mainly assembles LDHs on another substrate surface (such as $\alpha-Al_2O_3$, $\gamma-Al_2O_3$) that can provide the trivalent metal required for the reaction, and carry out the load growth. For instance, using an in-situ synthesis method, Mok *et al* used urea as a precipitant to load NiAl-LDHs on $\alpha-Al_2O_3$ [16]. When using this method to synthesize LDHs, the key thing is to adjust the pH of Al_2O_3 with alkaline substances such as ammonia to activate the Al source on the surface of Al_2O_3 to provide Al^{3+} for the nucleation of LDHs. The LDHs can be synthesized in situ on the surface of the Al_2O_3 carrier and in the pores. The mechanism is shown in Fig 3

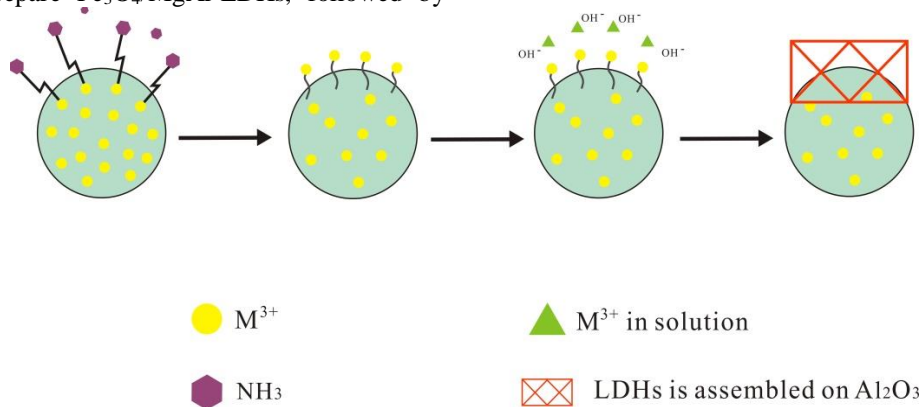


Fig. 3: Schematic illustration for in situ growth method.

In addition, Shao *et al* used Fe₃O₄ dispersed in a mixed solution of ethanol, deionized water and concentrated ammonia, and then added ethyl orthosilicate to prepare Fe₃O₄@SiO₂ microspheres. Then, AIOOH was assembled on the surface to prepare Fe₃O₄/SiO₂ microspheres[17]. Finally, Fe₃O₄@SiO₂@AIOOH was used to provide Al source, and Fe₃O₄@SiO₂@NiAl-LDHs were synthesized in-situ in a hydrothermal kettle with Ni(NO₃)₂·6H₂O and NH₄NO₃ at 100°C. The results revealed that the introduction of SiO₂ can make the AIOOH coating firmly fixed on the SiO₂ surface through hydrogen bonding. The Fe₃O₄@SiO₂@LDHs morphology is flower-like microspheres with uniform size and shape. Each LDHs grows vertically on the solid core like nanoplatelets and has good magnetic response capability. Moreover, Hui *et al* used this method to prepare Fe₃O₄@C@MgAl-LDH nanoparticles [18]. First, the sol-gel method was used to modify the surface of Fe₃O₄@C with AIOOH. Secondly, MgAl-LDHs was deposited on the surface of Fe₃O₄@C@AIOOH. The results demonstrated that the MgAl-LDHs sample had clear layered particles, and hexagonal plate crystallites grew on the surface of Fe₃O₄@C along staggered directions, with high dispersion and regular crystal shape.

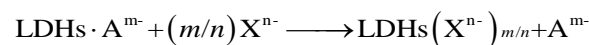
Furthermore, Yang *et al* grew MgAl-LDHs nanosheets in situ on the surface of Fe₃O₄@PDA (polydopamine) microspheres, and synthesized LDHs and PDA magnetic microspheres with different contents under the same conditions. SEM and TEM showed that Fe₃O₄@PDA@MgAl-LDHs has a core-shell structure, and the thickness of the PDA shell can be adjusted by controlling the mass ratio of Fe₃O₄ and PDA[19]. The peak of the nanocomposite with a mass ratio of Fe₃O₄/PDA and LDHs of 1:1 broadened significantly, which confirmed that the PDA shell layer participated in the structure of the nanocomposite.

The in-situ growth method can assemble Fe₃O₄@LDHs nanoparticles with high dispersion and regular crystal shape, but a substrate containing specific substances must be prepared in advance to ensure the normal supply of Al source. Therefore, the preparation process of this method is relatively complicated, and the requirements on the equipment are also relatively strict, which increases the assembling cost.

Ion exchange method

The ion exchange method comprises of co-precipitation and hydrothermal methods. The LDHs synthesized by co-precipitation and hydrothermal

methods utilize the exchangeability of anions between the plates to combine the target anions (such as drugs) with the anions between the LDHs. Exchange under certain conditions to obtain specific anion intercalation LDHs [19, 20]. Generally, high-valent anions are easy to exchange with low-valent anions between plates. This method is an important way to synthesize some special anion intercalation LDHs, and the intercalation anion needs to be able to exist stably. Generally, the ion exchange method can be carried out in the following way:



In this case, A^{m-} is the inter-plate anion, and Xⁿ⁻ is the target anion.

Nejati *et al* prepared nanocomposite CT-LDH/Fe₃O₄ by deposition of cetirizine (CT) intercalated Mg-Al layered double hydroxide (LDH) on Fe₃O₄ using a co-precipitation method [21]. The results showed that there were diffraction peaks of Fe₃O₄, CT and LDHs coexisting in CT-LDHs@Fe₃O₄. After intercalation, the interlayer spacing of LDHs increased from 0.88nm to 2.52nm, indicating that CT anions were successfully inserted into the interlayers of LDHs in the form of monolayers.

Secondly, Li *et al* used the same process to synthesize Fe₃O₄@Mg₃Al-LDHs with nitrate intercalation, and completed the intercalation of enrofloxacin (ENR) in a formamide solution[22]. The results showed that the interlayer nitrate ions of -LDHs can be substituted with ENR anions, and the Fe₃O₄@(ENR-LDHs) nanocomposite material obtained has notable superparamagnetism. Additionally, ENR anions are organized into a single layer between the layers of LDHs, and the interaction between the two is achieved through electrostatic attraction and hydrogen bonding.

L-Dopa (L-Dopa) can treat a variety of cancers, especially prostate and breast cancers. In order to achieve targeted drug delivery, Shahabadi *et al* prepared Fe₃O₄@CaAl-LDHs intercalated with carbonate ions by co-precipitation method, and then mixed with L-Dopa at pH=7.4 to obtain the product Fe₃O₄@CaAl-LDHs@L-Dopa[23]. The results showed that the synthesized drug particles are nearly spherical, with an average particle size of 120 nm, and the basal surface reflection of Fe₃O₄@CaAl-LDHs@L-Dopa is broadened. The ion exchange method provides a guiding method for preparing Fe₃O₄/LDHs with specific anions. The method is simple in process, but the anions have a competitive effect, and the target anions competes with the

interlayer anions or with other anions in the solution. Therefore, the ion exchange conditions are relatively harsh, which may result in low anion purity between the Fe₃O₄/LDHs plates prepared.

Thermal decomposition-reconstruction method

LDHs have a structural "memory effect" [24], which can be used to assemble the required anions between the layers of LDHs. Therefore, this method can be used to intercalate and prepare ions with weaker particle competitiveness, such as LDHs intercalated with nitrate ions, to obtain LDHs with high inter-plate ion purity.

Carja *et al* prepared MgFe-LDHs by co-precipitation method, and obtained FeO_x/Fe-LDHs after roasting. The samples were soaked in water, ethanol and aspirin solution to prepare aspirin intercalated LDHs [25]. Similarly, Pan *et al* co-precipitated calcined-reconstituted LDHs materials on the surface of Fe₃O₄ particles [26]. The uniformly dispersed magnetic Fe₃O₄@DFUR-LDHs particles containing the anticancer agent, doxyfluorouracil, were synthesized. The particles had a good core-shell structure and larger than the particle size of Fe₃O₄@LDO. The average particle size of the nearly monodisperse Fe₃O₄@DFUR-LDHs spherical sub-particles was about 300nm, which was close to the particle size range suitable for drug delivery. Furthermore, Li *et al* obtained chloride ion intercalation Fe₃O₄/ZnAl-LDHs by co-precipitation method, and used ferric ammonium citrate for ion exchange with chloride ions, and the resulting product was calcined as Fe₃O₄/LDO. The recovery was carried out in the mixed solution of HNO₃ and NaNO₃, and Fe₃O₄/ZnAl-LDHs with NO₃-intercalation were obtained [22].

The roasting recovery method can better solve the problem of anion competition, but the method needs to be carried out at a high temperature, and the roasting temperature needs to be strictly controlled to prevent the LDO structure from being damaged when the temperature is too high. At the same time, it is necessary to ensure the purity of the target anion solution. The outstanding advantage of this method is that it eliminates the competition between the target anion and other non-organic anions, but the preparation method is slightly more cumbersome than the ion exchange method. The gradual heating method during firing can improve the crystallinity of the LDO. If the heating speed is too fast or the firing temperature is too high, the escape of CO₂ and H₂O between the plates can cause the structure of

the LDO to be destroyed thus leading to lose of the "memory effect" [24].

Application of magnetic Fe₃O₄/LDHs nanoparticles

Catalytic performance

Photocatalytic performance

An important structural feature of the LDHs material is that its main structure is a MO₆ octahedron with two layers of brucite-like Mg(OH) co-edges. The cations such as M²⁺ and M³⁺ are uniformly distributed in the hydroxide layer. The high dispensability and the octahedral structure is an important factor affecting the photo-physical and photocatalytic properties of LDHs. Studies have shown that LDHs are a kind of "doped semiconductors" in which the "higher valence cations" act as dopants. This is because LDHs have 2 or 3 unique metal ions with a controllable ratio [27]. The change of transition metal ions in the brucite-like layer makes LDHs exhibit a wide range of photocatalytic properties, which is well reflected in photocatalytic applications [28, 29]. In addition, LDHs modified with precious metals such as Ag [30], Pt [31], and transition element oxides such as CeO₂ [32], TiO₂ [33], ZnO [34], are also used in the field of photocatalysis. Studies have shown that the modified LDHs particles may promote the electron-hole separation, thereby improving the catalytic capacity of the composite material.

The special properties of Fe₃O₄/LDHs have both adsorption capacity and photodegradation activity. During the entire preparation process, the adsorption and catalysis processes can be completed at the same time. Chen *et al* applied a 2-step microwave hydrothermal approach to make Fe₃O₄/ZnCr-LDHs composites [35]. Fe₃O₄ nanoparticles were dispersed on the surface of ZnCr-LDHs, the particle size was about 10nm, and there were numerous hydroxyl groups on the surface. Under ultraviolet light, the adsorption capacity of the composite material for methyl orange (MO) was 528 mg/g, and the degradation rate for methylene blue (MB) was 95%. Compared with ZnCr-LDHs under the same conditions, the composite material had a higher removal rate of dyes. This is due to coupling of Fe₃O₄ nanoparticles on the surface of ZnCr-LDHs

Sun *et al* used phosphate-intercalated LDHs as an intermediate medium to form Ag₃PO₄ on the surface of Fe₃O₄/LDHs microspheres [36], and successfully prepared a novel form of visible light-responsive photocatalyst Fe₃O₄@LDH@Ag/Ag₃PO₄

microspheres. This substance exhibited a highly effective visible light-based photocatalytic activity in breakdown of organic pollutants. In 5 consecutive cycles, the photocatalytic efficiency of Ag_3PO_4 decreased significantly, and the prepared $\text{Fe}_3\text{O}_4@LDHs@Ag/Ag_3PO_4$ sub-microspheres may be due to the combined effect of LDHs and Ag on the Ag_3PO_4 particles. After 5 cycles, the photocatalytic efficiency did not decrease significantly. Magnetic separation could also promote catalyst recovery, because magnetic separation exhibited a faster recovery time than centrifugal separation, and there was almost no catalyst loss during the recovery process.

Moreover, Huang *et al* used the in-situ growth method to prepare $\text{Fe}_3\text{O}_4@LDHs$ and FeS@LDHs for the breakdown of methoxychlor in the heterogeneous Fenton process [37]. The results showed that $\text{Fe}_3\text{O}_4@LDHs$ has a higher degradation activity than FeS@LDHs composites. This is due to ability of the composite material to generate hydroxyl radicals that can scavenge chlorides and oxidize methoxychlor. The optimal conditions for methoxychlor degradation was $\text{pH}=2.5-3.5$, the concentration of methoxychlor was 50~80 mg/L, AOT was 2.0g/L, and H_2O_2 dosage was 80 mmol/L. In the degradation process, $\text{Fe}_3\text{O}_4@LDHs$ Fenton system involve reductive dechlorination, cracking and oxidation reactions, while the $(\text{Fe}_3\text{O}_4+\text{FeS})@LDHs$ Fenton system leads to hydrogenolysis of FeS and cracking reactions.

Yang *et al* prepared $\text{Fe}_3\text{O}_4/\text{ZnAl-LDHs}$ using the sol-gel method, and prepared the $\text{Fe}_3\text{O}_4\text{-LDHs}/\text{TiO}_2$ modified with TiO_2 with different contents [38], and were named FLT-1, FLT-2 and FLT-5 (with TiO_2 content of 10%, 20% and 50%, respectively), and their photocatalytic removal of Cr(VI) ability was characterized. The results showed that FLT-2 exhibited better photocatalytic performance and excellent recycling performance. This is due to the fact that combination of $\text{Fe}_3\text{O}_4\text{-LDHs}$ and TiO_2 , by suppressing the photoelectric response and charge recombination in the EIS spectrum improves the electronic conductivity and photocatalytic performance. The results demonstrated that the $\text{Fe}_3\text{O}_4\text{-LDHs}/\text{TiO}_2$ composite material is one of the effective methods for the treatment of Cr(VI)-containing wastewater by the combination of adsorption and photocatalysis.

Recently, Shi *et al* developed an efficient and recyclable ternary magnetic $\text{Fe}_3\text{O}_4@ZnO/g\text{-C}_3\text{N}_4$ nanocomposites demonstrating excellent photocatalytic activity to methylene blue [39]. ZnO

nanoparticles anchored on the surface of Fe_3O_4 nanoparticles and $\text{Fe}_3\text{O}_4@ZnO$ existed on the surface of $g\text{-C}_3\text{N}_4$ formed $\text{Fe}_3\text{O}_4@ZnO/g\text{-C}_3\text{N}_4$ nanocomposites. The photocatalytic activity to MB of $\text{Fe}_3\text{O}_4@ZnO/g\text{-C}_3\text{N}_4$ nanocomposites was significantly higher than those of pristine $g\text{-C}_3\text{N}_4$ and $\text{Fe}_3\text{O}_4@ZnO$. The hydroxide and oxide radicals dominated the photocatalysis for the degradation of MB with $\text{Fe}_3\text{O}_4@ZnO/g\text{-C}_3\text{N}_4$ nanocomposites.

Catalytic organics

Besides being a catalyst for degradation of organic dyes, $\text{Fe}_3\text{O}_4/\text{LDHs}$ can also carry out catalytic reactions of organic substances through the loading, intercalation and assembly of metals and organic substances. For example, directly coated LDHs sheet-like nanocrystals perpendicular to the surface of Fe_3O_4 , and prepared a gold-loaded magnetic nanocatalyst $\text{Fe}_3\text{O}_4@MgAl\text{-LDHs}@Au$ by the deposition-precipitation technique, and used it to prepare 1-phenylethanol[40]. For the oxidation reaction, the catalyst has high 1-phenylethanol oxidation efficacy and can be easily separated by an external magnetic field. In addition, ICP confirmed that there was no leaching of Mg, Al and Au, in the supernatant after the reaction, while the SEM results of the recovered catalyst revealed that the morphology of Au and LDHs remained basically unchanged.

Kumar *et al* prepared $\text{Fe}_3\text{O}_4/\text{LDHs}$ magnetic nanoparticles in an alkali-free aqueous solution using O_2 as the oxidant and assembled the cobalt(II)-tetrasulfonic phthalocyanine (CoPcTs) and $\text{Fe}_3\text{O}_4/\text{LDHs}$ composite solid catalyst to catalyze mercaptans [41]. The basic centers on LDHs surface provide the covalent adsorption of CoPcTs active center. The catalyst showed good catalytic ability for deodorization of kerosene samples mixed with dodecyl mercaptan. After the reaction, an external magnet can be used to recover the catalyst from the reaction medium, and has a certain degree of reusability. Li *et al* fixed PdAu-PVP sol on the honeycomb core/shell carrier $\text{Fe}_3\text{O}_4@LDHs$, and prepared a series of core/shell structure catalysts PdAu/ $\text{Fe}_3\text{O}_4@LDHs$ by polyol reduction method [42]. This nanomaterial is used in the Heck reaction for the synthesis of variety of halogenated aromatic hydrocarbons and olefins. The amount of Au doping can effectively adjust particle size distribution, electron density and surface composition of the PdAu alloy on the catalyst.

Recently, Lin *et al* used ferric oxide (Fe_2O_3) and ferroferric oxide (Fe_3O_4) as catalysts on the pyrolysis products and the intrinsic reaction

mechanisms in a CO₂ atmosphere [43]. Carbon dioxide (CO₂) was introduced as the reaction atmosphere to further improve the quality of biofuel produced by microwave pyrolysis of food waste (FW). The results showed the biogas yield and the syngas concentration (H₂ + CO) increased to 70.34 wt% and 61.50 mol%, respectively, using Fe₃O₄ as the catalyst. The content of aliphatic hydrocarbons in bio-oil produced with the catalyst Fe₂O₃ increased to 67.48% and the heating value reached 30.45 MJ/kg.

Trans-esterification performance

The trans-esterification reaction is currently one of the effective ways to solve the fossil energy crisis. This method uses animal fats and vegetable oils as a catalyst under a heterogeneous solid base to perform the trans-esterification reaction to generate fatty acid methyl esters under relatively mild conditions (biodiesel) and glycerol [44]. Nowadays, there have been many examples of using LDO, a roasted product of LDHs, to prepare biodiesel, but it is difficult to remove the catalyst from the reaction system. Fe₃O₄/LDHs can better solve this problem [45].

Chen *et al* prepared Fe₃O₄/MgAl-LDHs and Zn-doped Fe₃O₄/ZnMgAl-LDHs by co-precipitation method [6]. After calcination, the layered structure of LDHs was destroyed to form a hydrotalcite-like solid base Fe₃O₄/MgAl-LDO and Fe₃O₄/ZnMgAl-LDO, and characterized their trans-esterification performance. The results showed that LDHs grown on the surface of Fe₃O₄ had better magnetic response ability. From the perspective of catalytic activity, the catalytic capability of Fe₃O₄/ZnMgAl-LDO is greater than that of Fe₃O₄/MgAl-LDO under the respective optimal reaction conditions. For the catalyst modified by Zn, Fe₃O₄/ZnMgAl-LDO with 15% Zn doping has the best catalytic activity. The analysis showed that this effect was due to the addition of Zn, which can effectively suppress the Jahn-Teller effect to a certain level, making the X-ray diffraction peaks of ZnMgAl-LDHs sharper and the layered structure tends to be complete. At the same time, it has a larger specific surface area than MgAl-LDHs. This series showed that the adding Zn improved the catalytic activity performance, which lead to an increase in catalytic efficiency.

Most recently, Liu *et al* developed magnetic whole-cell biocatalysts (MWCBS) by immobilizing *Bacillus subtilis* cells within ferro-ferric oxide-polyvinyl alcohol composite beads and utilized to transesterify waste frying oil to biodiesel in a magnetically fluidized bed reactor (MFBR) [46].

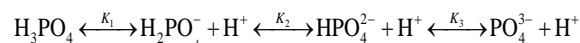
Response surface methodology and Box-Behnken design were employed to predict the optimal conditions. The maximum biodiesel yield reached 89.0 ± 0.6% after 48 h under the optimized conditions. MWCBS displayed satisfactory stability and reusability in MFBR.

Adsorption performance of Fe₃O₄/LDHs

Toxic metal ions produced by industrialization are usually released into the environment, thus making water pollution more and more serious. These metal elements pose a serious threat to people's lives [47, 48]. At the same time, dye materials discharged by industry are considered the number one pollutant of wastewater. Most dyes are essentially inert and non-biodegradable composed of synthetic aromatic compounds. Contaminated drinking water can cause cancer and mutagenesis [49]. The adsorptive properties of LDHs are derived from their "structural memory effect" and the anion exchange effect between the plates. Therefore, the adsorbent can be assembled by changing the type and quantity of ions between the LDHs plates. Studies have shown that LDHs have high adsorption potential for toxic dyes and metal ions, but separation and recovery are extremely challenging. Magnetic assisted adsorption separation technology is considered to be an effective method for separating powdery adsorbents from solutions. Therefore, the high-efficiency adsorption and recovery capacity of Fe₃O₄/LDHs have been widely reported.

Adsorption performance of ions in solution

Yan *et al* prepared 3 different magnetic core-shell composites, Fe₃O₄@MgAl-LDHs, Fe₃O₄@NiAl-LDHs and Fe₃O₄@ZnAl-LDHs by co-precipitation method [50], and studied their adsorption mechanism. Based on the 3 different Fe₃O₄@LDHs composite materials, removal efficiency of phosphorus decreased with the increase in pH. This may be related to the acidity and alkalinity of the phosphate species in the adsorbent surface and the solution at different pH values. It can be expressed as:



Thermodynamic analysis showed that the phosphate adsorption activity was intrinsically endothermic and spontaneous.

Using the same process, Koilraj *et al* prepared Fe₃O₄/Mg₂AlNO₃-LDHs magnetic composite material by co-precipitation method, and characterized its phosphate adsorption potential [10].

The results of this study demonstrated that as the adsorption progresses, partly, the phosphate was either co-precipitated with $\text{Al}(\text{OH})_3$ (at 25°C, $K_{\text{sp}}=1 \times 10^{-32}$) or AlPO_4 (at 25°C, $K_{\text{sp}}=6.3 \times 10^{-19}$). At higher pH values, the amount of phosphorus uptake decreased, which may be caused by increased charge of phosphate anion as a result of deprotonation, or competition of hydroxide anions in the reaction medium. In the presence of the same amount of carbonate, $\text{Fe}_3\text{O}_4/\text{Mg}_2\text{Al}(\text{OH})_6$ -LDHs reduced the adsorption of phosphate by about 50%, indicating that phosphate and carbonate are equally competitive with LDHs. In contrast, in presence of sulfate, adsorption of phosphate dominates. These materials are suitable for dephosphorization of sulfate-rich wastewater. The adsorption kinetics conforms to the quasi-second-order kinetics, and the adsorption isotherm conforms to the Langmuir single-layer adsorption model. In addition, removal of the adsorbent from the solution can be accomplished by using an external magnetic field.

Yang *et al* used in-situ growth technology to grow LDHs nanoparticles on the surface of Fe_3O_4 @PDA microspheres (MPL), and synthesized LDHs and polydopamine (PDA) microspheres with different contents under the same conditions and assessed its adsorption efficiency for U(VI) in aqueous solution [19]. The results revealed that the adsorption kinetics conformed to the quasi-two-stage model, and the adsorption rate of MP_2L_2 on U(VI) was as high as 94.8%. The adsorption capacity can be adjusted by modifying thickness of the PDA shell layer and levels of lactic acid. It is proved that PDA and LDH can provide a good adsorption platform for U(VI).

Li *et al* used the co-precipitation method to prepare three core-shell composite materials with MgAl-LDHs layer as the outer shell, SiO_2 matrix as the inner layer and Fe_3O_4 microspheres as the core [51]. These materials were used to remove and recycle phosphorus and fluorine in contaminated water. The produced mesoporous Fe_3O_4 @ SiO_2 @MgAl-LDHs composite material had a good magnetic separability and uniform pore distribution. Due to the mesoporous structure, the MgAl-LDHs composite material demonstrated an excellent adsorption capacity for fluoride and phosphate, easy to be magnetically removed from the solution, regenerated and reused after a simple treatment.

Recently, Xu *et al* studied the application of bifunctional polysilsesquioxane/carbon nanotube magnetic composites in the adsorption of Au (III) ions [52]. The bifunctional magnetic composites were prepared by coating the polysilsesquioxane with

amino and thiol groups on carboxyl carbon nanotubes (CNTs-COOH) embedded with magnetic ferro-ferric oxide (Fe_3O_4). The adsorption capacities of the composites for Au(III) at 35 °C varied from 2.01 mmol/g to 2.82 mmol/g according to the Langmuir model. Selective adsorption tests showed that the bifunctional composites could selectively adsorb Au(III) in a number of binary metal ions systems.

The adsorption performance of organic matter

Lu *et al* prepared Fe_3O_4 @MgAl-LDHs by the co-precipitation method, which has a layered porous structure with platelet-wrapped morphology in vertical/tilted/horizontal orientation, to effectively remove anionic dye in wastewater. This three-dimensional layered porous structure lead to a high adsorption capacity for anionic dye (maximum adsorption level is beyond 810mg/g) [53]. The results of this study revealed that the adsorption activity conformed to the Langmuir monolayer model, and the adsorption mechanism was mainly electrostatic adsorption and anion exchange. The adsorbed magnetic microspheres were easily removed from the aqueous medium, and the adsorbent regeneration could be accomplished using methanol solution. Therefore, Fe_3O_4 @MgAl-LDHs can be utilized to effectively adsorb acid dyes in water.

In addition, Li *et al* prepared a core-shell magnetic rhamnolipid-derived magnetic adsorbent Fe_3O_4 @(RL-LDH) using a layering/recombination method, which can efficiently get rid of p-cresol/hydroquinone from heavy metal-phenolic pollutants in aqueous solution [42]. The adsorption of p-cresol and hydroquinone on the adsorbent reached equilibrium at approximately 140 minutes and 200 minutes, correspondingly, and the adsorption kinetics is a quasi-two-stage kinetic model, which can be easily recovered using an external magnetic field within 20s.

Hou *et al* used electrostatic interaction to prepare $\text{Fe}_3\text{O}_4/\text{MgAl-LDHs}$ and $\text{Fe}_3\text{O}_4/\text{MgAl-LDO}$ nanocomposites for the adsorption of graphene oxide (GO) in aqueous medium [15]. The maximum adsorption capacities of $\text{Fe}_3\text{O}_4/\text{MgAl-LDHs}$ and $\text{Fe}_3\text{O}_4/\text{MgAl-LDO}$ for GO was 82.4 mg/g and 86.7 mg/g, respectively. The adsorption capacity of MLDH/MLDO on GO was largely determined by surface complexation and electrostatic interaction. It was separated by the magnet within 10s after adsorption. The adsorption kinetics data followed the quasi-second-order equation, and the adsorption isotherm fit the Freundlich and Langmuir isotherms.

Most recently, Weng *et al* demonstrated the effectiveness of cobalt-based zeolitic imidazole frameworks (ZIF-67) coated biosynthesized ferroferric oxide@silicon dioxide ($\text{Fe}_3\text{O}_4@\text{SiO}_2$) magnetic composite ($\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{ZIF-67}$) in removing doxorubicin hydrochloride (DOX) from wastewater [54]. The fabricated composite had a large specific surface area ($501.9 \text{ m}^2/\text{g}^{-1}$) which contributed to a high DOX removal efficiency (90.7%) and elevated DOX removal amount ($90.7 \text{ mg}/\text{g}^{-1}$) higher than the composite's constituent parts. Adsorption followed pseudo-second-order kinetics, where DOX adsorption best fit the Langmuir isotherm model. Furthermore, a possible adsorption mechanism of DOX by $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{ZIF-67}$ was also proposed which suggested that a combination of different processes collective led to efficient DOX removal.

Medical applications

The magnetic targeted therapy delivery system was postulated by [55]. The system consists of drugs, magnetic materials, carrier constituents, among other components. Through this system, drugs can be targeted to the ill part of the body using an external magnetic field avoiding phagocytosis by the reticuloendothelial system. This system can increase local drug dose, improve drug selectivity and decrease drug toxicity [56]. Among nanomaterials, LDHs have been broadly applied in the field of biomedicine due to their layered structure and due to their low toxicity and better biocompatibility [57].

Application in the treatment of malignant tumors

Cancer is one of the deadliest disease in the world. Radiotherapy, chemotherapy and thermochemotherapy are the main clinical treatments for cancer. Radiotherapy uses high-energy radiation to damage or induce cell cycle arrest in cancer cells. However, chemotherapy involves the use of various chemicals alone or in large amounts to kill tumor cells. However, these chemicals kill normal cells during the treatment and affect the normal life of the patient. Thermochemotherapy uses the difference between the heat resistance of normal cells and cancer cells in the human body. It uses energy such as alternating magnetic field to heat the drug in the outside world to maintain the temperature at a certain threshold. At this temperature, it can kill tumor cells and without damaging the normal tissues [58]. $\text{Fe}_3\text{O}_4/\text{LDHs}$ has a certain threshold temperature, under which thermochemotherapy and drug release can work. Based on this unique characteristic, people have explored $\text{Fe}_3\text{O}_4/\text{LDHs}$ as a "release switch" [59].

Komarala *et al* prepared $\text{Fe}_3\text{O}_4/\text{MgAl-LDHs}$ by electrostatic interaction method [60]. The results showed that doxorubicin was successfully intercalated into $\text{Fe}_3\text{O}_4/\text{MgAl-LDHs}$ nano-hybrid materials. At the same time, the introduction of Fe_3O_4 acted as a "cut-off switch". $\text{Fe}_3\text{O}_4@\text{MgAl-LDHs}$ loaded with doxorubicin can increase the temperature of the suspension from room temperature within 10 minutes by exposing it to an alternating magnetic field with an intensity of 376 Oe. Up to 45°C , the temperature is fatal to cancer cells, but not harmful to tumor cells. With the extension of the treatment time, the number of viable cells decreased exponentially. Even a 10-minute treatment time was enough to reduce the number of viable cells by 60%. In addition, this effect of thermochemotherapy on cell viability reached saturation at about 20 minutes.

Methotrexate (MTX) is a stoichiometric inhibitor of dihydrofolate reductase, which can effectively treat certain cancers, such as breast cancer, skin cancer, lung cancer and other malignant tumors [61, 62]. Zhao *et al* prepared $\text{Fe}_3\text{O}_4/\text{LDHs}$ nanoparticles by hydrothermal method, and prepared almost monodisperse magnetic $\text{Fe}_3\text{O}_4/\text{LDHs-MTX-Au}$ system by ion exchange method [59]. These particles have a good core-shell structure, and Au ions are dispersed on the surface of $\text{Fe}_3\text{O}_4/\text{LDHs-MTX}$. The results indicated that the release behavior was due to the rearrangement of magnetic particles caused by magnetically induced aggregation. Under acidic conditions, MTX can be effectively released from the system through the combined action of the dissolution of the LDHs layer and ion exchange. The free MTX quickly reached the equilibrium within 120 minutes, and almost 100% was released. In the absence of an external magnetic field mode, the $t_{0.5}$ (half release time) of $\text{Fe}_3\text{O}_4@\text{MTX-LDHs}/\text{Au}$ (sample a) was 24 minutes, and the release rate of MTX after 200 minutes was 91.0%. Completely different from sample a, the release curve of MTX in $\text{Fe}_3\text{O}_4@\text{MTX-LDH}/\text{Au}$ in sample b under an external magnetic field of 0.1T showed that $t_{0.5}$ was 88min, and the equilibrium release percentage greater than 500min was only 67.0%. The release rate was significantly slower than that of sample a. The cell viability test showed that the cell viability histogram of MTX and Fe_3O_4 decreased slowly, and the cell viability histogram of $\text{Fe}_3\text{O}_4@\text{MTX-LDHs}/\text{Au}$ nanoparticles decreased faster. Therefore, this new approach can be much more effective in inhibiting cancer cells than MTX itself.

Carlino *et al* prepared $\text{Fe}_3\text{O}_4/\text{CaAl-LDHs}$ by co-precipitation method and completed the assembly of L-Dopa (levodopa) [24]. The results showed that the L-Dopa (levodopa) molecule interacted with the

LDHs layer mainly through static electricity, hydrogen bonds and *van der Waals* forces. The release characteristics of $\text{Fe}_3\text{O}_4/\text{CaAl-LDHs}$ were better at $\text{pH}=5.5$, and the release rate was significantly reduced at higher pH ($\text{pH}=7.4$). This was due to a decrease in the pH of the aqueous solution which in turn increased the solubility of L-Dopa. At the same time, a decrease in pH led to the protonation of amino and hydroxyl groups and weaken the drug/carrier interaction, thereby increasing the release of L-Dopa. Studies have shown that the extracellular pH of tumor tissue is usually acidic. Therefore, $\text{Fe}_3\text{O}_4/\text{CaAl-LDHs}$ can be used as an ideal pH -responsive carrier for L-Dopa.

Recently, Chen *et al* developed a nanoplatform consisting of a therapeutic core containing ferro-ferric oxide nanoparticles, calcium peroxide and paclitaxel (PTX, anticancer drug), as well as a bilayer shell containing thermal-responsive lauric acid (LA) and tumor targeted hyaluronic acid (HA) [63]. After injection, the HA segment first guided the nanoplatform to tumor tissue, allowing the further tumor specific therapy. Subsequently, the LA shell on the accumulated nanoplatform switched from solid to liquid under near-infrared radiation, which further exposed the preloaded cargos (CaO_2 NPs, Fe_3O_4 NPs and PTX), resulting in CaO_2 induced $\text{H}_2\text{O}_2/\text{O}_2$ generation for inhibition of hypoxia-dependent drug resistance, Fe_3O_4 catalyzed hydroxyl radical production for catalytic medicine and to near-infrared triggered PTX release for chemotherapy.

Application of targeted therapy

New biocompatible targeted delivery drugs with adsorption-desorption properties have been widely studied. With the advancement of technology, studies on the use of nano-based materials as delivery vehicles for drugs to the targeted cells has increased. Among the various nano materials used, $\text{Fe}_3\text{O}_4/\text{LDHs}$ is highly favored due to the following advantages: (i) The targeted delivery of drugs can be accomplished with the help of an external magnetic field, (ii) It can reduce the content of drugs that need to be delivered to reach a specific concentration, (iii) It can reduce the concentration of drugs in non-target locations.

For instance, Li *et al* prepared $\text{Fe}_3\text{O}_4@DFUR\text{-MgAl-LDHs}$ intercalated with DFUR (doxyfluorouracil reagent) on the surface of Fe_3O_4 spherical particles by co-precipitation-calcination-reconstruction method [27]. Under the condition of $37.5\pm 0.5^\circ\text{C}$, the magnetron drug release ability of DFUR from $\text{Fe}_3\text{O}_4@DFUR\text{-LDHs}$ is characterized in

the "MF on" (that is; external magnetic field) and "MF off" (that is; no external magnetic field) modes. The results showed that in the "MF off" mode, $\text{Fe}_3\text{O}_4@DFUR\text{-LDHs}$ could release half of the drug in 20 minutes, and it took 200 minutes to release 96.0% of DFUR. In the "MF on" mode (magnetic field of 0.15 T), the release rate of DFUR in $\text{Fe}_3\text{O}_4@DFUR\text{-LDHs}$ over 560 minutes was only 93.0%, which was significantly lower than that in the "MF off" mode. This effect was due to rearrangement of magnetic particles induced by magnetic force, indicating that this kind of magnetic particles could be used for drug release.

Bi *et al* used the double-drop co-precipitation method to assemble ZnAl-LDHs intercalated with salicylate (SA) with different growth orientations on the surface of Fe_3O_4 sub-microspheres with a diameter of about 480 nm [64]. The results revealed that under the condition of "MF off", all the curves showed a rapid release in the initial 15 minutes, followed by a slow and stable release phase, until it reached a constant value for 7.5 hours. Likewise, in the "MF on" mode, all magnetic nano-carriers exhibited a detectable slower SA release rate. This could be attributed to the particle-particle interaction between the magnetic nano-carriers. The kinetic fitting showed that the release behavior of all samples involved bulk diffusion and surface diffusion processes.

Furthermore, Li *et al* prepared $\text{Fe}_3\text{O}_4@MgAl\text{-LDHs}$ by co-precipitation method, and intercalated and assembled ENR (enrofloxacin) by ion exchange method to synthesize $\text{Fe}_3\text{O}_4@(ENR\text{-LDHs})$ [65]. The results showed that when ENR and $\text{Fe}_3\text{O}_4/\text{LDHs}$ were physically mixed, the release rate was 86.26% at the time of 26 minutes and $\text{pH}=4.6$; the release rate was 80.75% at the time of 36 minutes and $\text{pH}=7.2$. However, at $\text{pH}=4.6$ and 7.2, $\text{Fe}_3\text{O}_4@(ENR\text{-LDHs})$ showed a gradual release over time. Under the conditions of $\text{pH}=4.6$ and $\text{pH}=7.2$, there was a burst release of about 58% and 43% respectively at 5 minutes. This might be related to the loss of ENR adsorption on the surface of LDHs and the poor intercalation of ENR, resulting to the slow-release effect. At $\text{pH}=4.6$, the sustained-release equilibrium was reached at 220 minutes, and 85% of ENR was released. At $\text{pH}=7.2$, the sustained-release equilibrium was reached at 430 min, and about 86% of ENR was released. This study revealed that the slow-release process of ENR from $\text{Fe}_3\text{O}_4@(ENR\text{-LDHs})$ was due to slow ion exchange process between ENR anions and anions in the buffer.

Table-1: Synthesis and application of selected magnetic Fe₃O₄/LDHs nanoparticles.

Nanocomposite	Synthesized method	Anion	Applications	References
Fe ₃ O ₄ /ZnCr	two-step microwave hydrothermal method	-	Adsorption of methyl orange	[14]
Ab ₂ /Fc- NiAl@ Fe ₃ O ₄	Co-precipitation synthesis and Ion-exchange	FC	Electrochemical immunoassay	[66]
Fe ₃ O ₄ /MgAl	Electrostatic action	NO ₃ ⁻	Adsorption of As(III)	[67]
Fe ₃ O ₄ /MgAl	Co-precipitation synthesis	CO ₃ ²⁻	Adsorption of Cd(II)	[68]
Fe ₃ O ₄ /MgAl	Electrostatic action	CO ₃ ²⁻	Adsorption of Cd(II)	[69]
Fe ₃ O ₄ @C/MgAl	In situ growth	CO ₃ ²⁻	Adsorption of Cd(II)	[18]
Fe ₃ O ₄ @MgAl-MTX	Hydrothermal method and Ion-exchange	MTX	Targeted cancer therapy	[70]
Fe ₃ O ₄ @Al ₂ O ₃ @ZnFe	Co-precipitation synthesis	CO ₃ ²⁻	Adsorption of As	[71]
Fe ₃ O ₄ /MgAl	Electrostatic action	CO ₃ ²⁻	anti-ultraviolet aging and microwave absorption properties	[67]
Fe ₃ O ₄ /Zn-Al	Electrostatic action	NO ₃ ⁻	Removal of naphthalene	[72]
Fe ₃ O ₄ /Zn-Al-Fe-La	Co-precipitation synthesis	SO ₄ ²⁻	Removal of PO ₄ ³⁻	[73]
MCs@Mg/Fe-LDHs	Co-precipitation synthesis	CO ₃ ²⁻	removal of Pb(II) and Cu(II)	[8]
Fe ₃ O ₄ @ZnAl	Co-precipitation synthesis	CO ₃ ²⁻	Determination of phenoxy acid herbicides	[2]

Conclusions

The synthesis and application of novel nano-based materials is rapidly increasing. The advancement in nanotechnology has led to synthesis of nanomaterials with mixed compositions thus widening their scope of application in different fields. This article reviews research progress on the synthesis and application of LDHs-based magnetic nanocomposite functional materials Fe₃O₄/LDHs. Even though different Fe₃O₄/LDHs particles suitable for various fields have been prepared, the micro-control mechanism of Fe₃O₄/LDHs is not clear yet. Therefore, future research need to be carried to further understand the mechanism of action of Fe₃O₄/LDHs functional nanomaterials, consequently increasing their industrial applications.

Declaration of Competing Interests

The authors declare no competing interests.

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