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 [M₁₂−2xMₓ(OH)₆]ⁿ⁺, [Aₓ/ₙ]ⁿ⁻ · mH₂O, where M is the divalent and trivalent metal ions, respectively. A⁻ denotes the interlayer anions that balance the positive charges on the layers, and x is defined as the molar ratio of M²⁺ to (M²⁺ + M³⁺). Therefore, LDHs are positively charged substances, which is caused by the isomorphous replacement of M²⁺ to M³⁺ 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 O₂− 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 O₂− in the middle, and neighboring electrons jump back and forth between the transfers of O₂−. 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) Poses 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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The co-precipitation technique involves the addition of M$^{2+}$ and M$^{3+}$ dropwise 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$_3$O$_4$. Therefore, it is easier to obtain Fe$_3$O$_4$/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 Fe$_3$O$_4$/LDO by roasting, it is necessary to add certain protective measures such as nitrogen protection to prevent crystal phase transformation of Fe$_3$O$_4$ and other crystals added Fe$_3$O$_4$ 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$_2$CO$_3$ as precipitating agents to maintain the pH at around 10, Al(NO$_3$)$_3$·9H$_2$O and Mg(NO$_3$)$_2$·6H$_2$O were precipitated to produce Fe$_3$O$_4$/MgAl-LDHs. In addition, Koilraj et al used the co-precipitation method to synthesize nitrate-intercalation by using Fe$_3$O$_4$ 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 Fe$_3$O$_4$/Mg$_2$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$_3$O$_4$ suspension, and prepared Fe$_3$O$_4$ with a mixed solution of 1M NaOH and 0.5M NaHCO$_3$ under the condition of pH=10 and prepared Fe$_3$O$_4$/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 Fe$_3$O$_4$/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 Fe$_3$O$_4$/LDHs. Under the combined action of proper particle concentration and solvent effect, metal ions rapidly adsorb on negatively charged Fe$_3$O$_4$ surface effectively inducing LDHs microcrystals to nucleate on the Fe$_3$O$_4$ surface and grow slowly and vertically. Zhao et al used water and methanol-water as dispersants to disperse Fe$_3$O$_4$, and prepared Fe$_3$O$_4$@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 Fe$_3$O$_4$ sub-microspheres, with strong magnetization, particularly the composite material obtained in water media was honeycomb-shaped, staggered on the Fe$_3$O$_4$ surface [12]. Similarly, Zhang et al used the same method to prepare Fe$_3$O$_4$@CuMgAl-LDHs by dispersing Fe$_3$O$_4$ into methanol solutions of different concentrations[13]. The vibrating sample magnetometer results demonstrated that all samples displayed superparamagnetism. The magnetic saturations of Fe$_3$O$_4$@CuMgAl-2 and Fe$_3$O$_4$@CuMgAl-1 reduced to 60.5 and 51.0emu·g$^{-1}$, respectively, while Fe$_3$O$_4$ 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$_2$O$_3$ 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$_2$O$_3$/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$_2$O$_3$/LDHs.

Chen et al dispersed 0.2 g of Fe$_2$O$_3$ into Cr(NO$_3$)$_3$.9H$_2$O and Zn(NO$_3$)$_2$.6H$_2$O solutions and adjusted the pH with NH$_3$·H$_2$O [14]. With the aid of microwave, Fe$_2$O$_3$/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$_3$.6H$_2$O and after the mixture was uniformly mixed[15], 20 mL of ethylenediamine, 6.0 g of CH$_3$COONa·3H$_2$O 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$_2$O$_3$/MgAl-LDHs, followed by calcination at 500 °C to obtain Fe$_2$O$_3$/MgAl-LDO. The results showed that Fe$_2$O$_3$/MgAl-LDHs had the characteristic structure of lamellar platelets. The presence of uneven dark spots (Fe$_2$O$_3$) indicated that the prepared material was a composite of MgAl-LDHs and Fe$_2$O$_3$. After calcination, compared with Fe$_2$O$_3$/MgAl-LDHs, Fe$_2$O$_3$/MgAl-LDO had a smaller size and smooth edges. The lattice spacing of Fe$_2$O$_3$/MgAl-LDHs and Fe$_2$O$_3$/MgAl-LDO were 0.206nm and 0.252nm, respectively. Infrared showed that Fe$_2$O$_3$/MgAl-LDHs had a large number of hydroxyl vibration peaks, and the hydroxyl vibration peaks of Fe$_2$O$_3$/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$_2$O$_3$/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 α-Al$_2$O$_3$, γ-Al$_2$O$_3$) 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 α-Al$_2$O$_3$[16]. When using this method to synthesize LDHs, the key thing is to adjust the pH of Al$_2$O$_3$ with alkaline substances such as ammonia to activate the Al source on the surface of Al$_2$O$_3$ to provide Al$^{3+}$ for the nucleation of LDHs. The LDHs can be synthesized in situ on the surface of the Al$_2$O$_3$ carrier and in the pores. The mechanism is shown in Fig 3.

![Fig. 3: Schematic illustration for in situ growth method.](image)
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, AlOOH was assembled on the surface to prepare Fe₃O₄@SiO₂@AlOOH microspheres[17]. Finally, Fe₃O₄@SiO₂@AlOOH 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 AlOOH 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 AlOOH. Secondly, MgAl-LDHs was deposited on the surface of Fe₃O₄@C@AlOOH. 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 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:

\[ \text{LDHs} \cdot A^{m-} + (m/n)X^o \longrightarrow \text{LDHs}(X^o)^{m/n} + A^{m-} \]

In this case, A^{m-} is the inter-plate anion, and X^o 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@MgₓAl-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@MgₓAl-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 Fe\(_2\)O\(_4\)/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 FeOx/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 Fe\(_2\)O\(_4\) particles[26]. The uniformly dispersed magnetic Fe\(_2\)O\(_4\)@DFUR-LDHs particles containing the anticancer agent, doxifluorouracil, were synthesized. The particles had a good core-shell structure and larger than the particle size of Fe\(_2\)O\(_4\)@LDO. The average particle size of the nearly monodisperse Fe\(_2\)O\(_4\)@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 Fe\(_2\)O\(_4\)/ZnAl-LDHs by co-precipitation method, and used ferric ammonium citrate for ion exchange with chloride ions, and the resulting product was calcined as Fe\(_2\)O\(_4\)/LDO. The recovery was carried out in the mixed solution of HNO\(_3\) and NaNO\(_3\), and Fe\(_2\)O\(_4\)/ZnAl-LDHs with NO\(_3\)-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 CO\(_2\) and H\(_2\)O 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 Fe\(_2\)O\(_4\)/LDHs nanoparticles**

**Catalytic performance**

**Photocatalytic performance**

An important structural feature of the LDHs material is that its main structure is a MO\(_6\) octahedron with two layers of brucite-like Mg(OH) co-edges. The cations such as M\(^{2+}\) and M\(^{3+}\) 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 CeO\(_2\) [32], TiO\(_2\) [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 Fe\(_2\)O\(_4\)/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 Fe\(_2\)O\(_4\)/ZnCr-LDHs composites[35], Fe\(_2\)O\(_4\) nanoparticles were dispersed on the surface of ZnCr-LDHs, the particle size was about 10nm, and there were numerous hydroxy 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 Fe\(_2\)O\(_4\) nanoparticles on the surface of ZnCr-LDHs.

Sun et al used phosphate-intercalated LDHs as an intermediate medium to form Ag\(_3\)PO\(_4\) on the surface of Fe\(_2\)O\(_4\)/LDHs microspheres [36], and successfully prepared a novel form of visible light-responsive photocatalyst Fe\(_2\)O\(_4\)@LDH@Ag@Ag\(_3\)PO\(_4\).

**References**


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 Ag₃PO₄ decreased significantly, and the prepared Fe₃O₄@LDHs@Ag/Ag₃PO₄ sub-microspheres may be due to the combined effect of LDHs and Ag on the Ag₃PO₄ 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 Fe₃O₄@LDHs and FeS@LDHs for the breakdown of methoxychlor in the heterogeneous Fenton process [37]. The results showed that Fe₃O₄@LDHs has a higher degradation activity than FeS@LDHs composites. This is due to the ability of the composite material to generate hydroxyl radicals that can scavenge chlorides and oxidize methoxychlor. The optimal conditions for methoxychlor degradation was pH=2.5-3.5, the concentration of methoxychlor was 50~80 mg/L, and H₂O₂ dosage was 80 mmol/L. In the degradation process, Fe₃O₄@LDHs Fenton system involve reductive dechlorination, cracking and oxidation reactions, while the (Fe₃O₄+FeS)@LDHs Fenton system leads to hydrogenolysis of FeS and cracking reactions.

Yang et al. prepared Fe₃O₄/ZnAl-LDHs using the sol-gel method, and prepared the Fe₃O₄@LDHs/TiO₂ modified with TiO₂ with different contents [38], and were named FLT-1, FLT-2 and FLT-5 (with TiO₂ 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 Fe₃O₄@LDHs and TiO₂, by suppressing the photoelectric response and charge recombination in the EIS spectrum improves the electronic conductivity and photocatalytic performance. The results demonstrated that the Fe₃O₄@LDHs/TiO₂ 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 Fe₃O₄/ZnO@g-C₃N₄ nanocomposites demonstrating excellent photocatalytic activity to methylene blue [39]. ZnO nanoparticles anchored on the surface of Fe₃O₄ nanoparticles and Fe₃O₄/ZnO existed on the surface of g-C₃N₄ formed Fe₃O₄@ZnO@g-C₃N₄ nanocomposites. The photocatalytic activity to MB of Fe₃O₄@ZnO@g-C₃N₄ nanocomposites was significantly higher than those of pristine g-C₃N₄ and Fe₃O₄@ZnO. The hydroxide and oxide radicals dominated the photocatalysis for the degradation of MB with Fe₃O₄@ZnO@g-C₃N₄ nanocomposites.

Catalytic organics

Besides being a catalyst for degradation of organic dyes, Fe₃O₄/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 Fe₃O₄, and prepared a gold-loaded magnetic nanocatalyst Fe₃O₄@MgAl-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 Fe₃O₄/LDHs magnetic nanoparticles in an alkali-free aqueous solution using O₂ as the oxidant and assembled the cobalt(II)-tetrakisphthalocyanine (CoPcTs) and Fe₃O₄/LDHs composite solid catalyst to catalyze mercaptans [41]. The basic centers on LDHs surface provide the covalent adsorption of CoPcTs active centers. The catalyst showed good catalytic ability for deodorization of kerosene samples mixed with dodecyl mercapatan. 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 Fe₃O₄@LDHs, and prepared a series of core/shell structure catalysts PdAu/Fe₃O₄@LDHs by polyol reduction method [42]. This material is used in the Heck reaction for the synthesis of various 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 (Fe₂O₃) and ferroferric oxide (Fe₃O₄) as catalysts on the pyrolysis products and the intrinsic reaction...
mechanisms in a CO\textsubscript{2} atmosphere [43]. Carbon dioxide (CO\textsubscript{2}) 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 (H\textsubscript{2} + CO) increased to 70.34 wt% and 61.50 mol%, respectively, using Fe\textsubscript{3}O\textsubscript{4} as the catalyst. The content of aliphatic hydrocarbons in bio-oil produced with the catalyst Fe\textsubscript{3}O\textsubscript{4} 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. Fe\textsubscript{3}O\textsubscript{4}/LDHs can better solve this problem [45].

Chen et al prepared Fe\textsubscript{3}O\textsubscript{4}/MgAl-LDHs and Zn-doped Fe\textsubscript{3}O\textsubscript{4}/ZnMgAl-LDHs by co-precipitation method [6]. After calcination, the layered structure of LDHs was destroyed to form a hydrotalcite-like solid base Fe\textsubscript{3}O\textsubscript{4}/MgAl-LDO and Fe\textsubscript{3}O\textsubscript{4}/ZnMgAl-LDO, and characterized their trans-esterification performance. The results showed that LDHs grown on the surface of Fe\textsubscript{3}O\textsubscript{4} had better magnetic response ability. From the perspective of catalytic activity, the catalytic capability of Fe\textsubscript{3}O\textsubscript{4}/ZnMgAl-LDO is greater than that of Fe\textsubscript{3}O\textsubscript{4}/MgAl-LDO under the respective optimal reaction conditions. For the catalyst modified by Zn, Fe\textsubscript{3}O\textsubscript{4}/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 Fe\textsubscript{3}O\textsubscript{4}/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 Fe\textsubscript{3}O\textsubscript{4}/LDHs have been widely reported.

Adsorption performance of ions in solution

Yan et al prepared 3 different magnetic core-shell composites, Fe\textsubscript{3}O\textsubscript{4}@MgAl-LDHs, Fe\textsubscript{3}O\textsubscript{4}@NiAl-LDHs and Fe\textsubscript{3}O\textsubscript{4}@ZnAl-LDHs by co-precipitation method [50], and studied their adsorption mechanism. Based on the 3 different Fe\textsubscript{3}O\textsubscript{4}@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:

\[\text{H}_3\text{PO}_4^- \rightleftharpoons \text{H}_2\text{PO}_4^- + \text{H}^+ \rightleftharpoons \text{HPO}_4^{2-} + \text{H}^+ \rightleftharpoons \text{PO}_4^{3-} + \text{H}^+\]

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

Using the same process, Koilraj et al prepared Fe\textsubscript{3}O\textsubscript{4}/Mg\textsubscript{3}AlNO\textsubscript{3}-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 Al(OH)₃ (at 25°C, Ksp=1×10⁻32) or AlPO₄ (at 25°C, Ksp=6.3×10⁻19). 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, Fe₃O₄/Mg₂AlNO₃-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 Fe₃O₄@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 MP₂L₂ 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, SiO₂ matrix as the inner layer and Fe₃O₄ microspheres as the core [51]. These materials were used to remove and recycle phosphorus and fluoride in contaminated water. The produced mesoporous Fe₃O₄@ SiO₂@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 biofunctional 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 (Fe₃O₄). 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 Fe₃O₄@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, Fe₃O₄@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 Fe₃O₄@(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 Fe₃O₄/MgAl-LDHs and Fe₃O₄/MgAl-LDO nanocomposites for the adsorption of graphene oxide (GO) in aqueous medium [15]. The maximum adsorption capacities of Fe₃O₄/MgAl-LDHs and Fe₃O₄/MgAl-LDO for GO was 82.4 mg/g and 86.7 mg/g, respectively. The adsorption capacity of MLDH/MLDGO on GO was largely determined by surface complexion 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 (Fe₃O₄@SiO₂) magnetic composite (Fe₃O₄@SiO₂/ZIF-67) in removing doxorubicin hydrochloride (DOX) from wastewater [54]. The fabricated composite had a large specific surface area (501.9 m²/g) which contributed to a high DOX removal efficiency (90.7%) and elevated DOX removal amount (90.7 mg/g) 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 Fe₃O₄@SiO₂/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 diseases 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]. Fe₃O₄/LDHs has a certain threshold temperature, under which thermochemotherapy and drug release can work. Based on this unique characteristic, people have explored Fe₃O₄/LDHs as a “release switch” [59].

Komarala et al prepared Fe₃O₄/MgAl-LDHs by electrostatic interaction method [60]. The results showed that doxorubicin was successfully intercalated into Fe₃O₄/MgAl-LDHs nano-hybrid materials. At the same time, the introduction of Fe₃O₄ acted as a “cut-off switch”. Fe₃O₄/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 Fe₃O₄/LDHs nanoparticles by hydrothermal method, and prepared almost monodisperse magnetic Fe₃O₄/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 Fe₃O₄/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 t₀.₅ (half release time) of Fe₃O₄@MTX-LDHs/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 Fe₃O₄@MTX-LDH/Au in sample b under an external magnetic field of 0.1T showed that t₀.₅ was 88 min, and the equilibrium release percentage greater than 500 min 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 Fe₃O₄ decreased slowly, and the cell viability histogram of Fe₃O₄@MTX-LDHs/Au nanoparticles decreased faster. Therefore, this new approach can be much more effective in inhibiting cancer cells than MTX itself.

Carlino et al prepared Fe₃O₄/CoAl-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 Fe$_3$O$_4$/CaAl-LDHs were better at pH=5.5, and the release rate was significantly reduced at higher pH (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, Fe$_3$O$_4$/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$_3$O$_4$ NPs and PTX), resulting in CaO$_2$ induced H$_2$O$_2$/O$_2$ generation for inhibition of hypoxia-dependent drug resistance, Fe$_3$O$_4$ 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, Fe$_3$O$_4$/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 Fe$_3$O$_4$@DFUR-MgAl-LDHs intercalated with DFUR (doxyfluorouracil reagent) on the surface of Fe$_3$O$_4$ spherical particles by co-precipitation-calcination-reconstruction method [27]. Under the condition of 37.5±0.5°C, the magnetron drug release ability of DFUR from Fe$_3$O$_4$@DFUR-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, Fe$_3$O$_4$@DFUR-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 Fe$_3$O$_4$@DFUR-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$_3$O$_4$ 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 Fe$_3$O$_4$@MgAl-LDHs by co-precipitation method, and intercalated and assembled ENR (enrofloxacin) by ion exchange method to synthesize Fe$_3$O$_4$@([ENR-LDHs] [65]. The results showed that when ENR and Fe$_3$O$_4$/LDHs were physically mixed, the release rate was 86.26% at the time of 26 minutes and pH=4.6; the release rate was 80.75% at the time of 36 minutes and pH=7.2. However, at pH=4.6 and 7.2, Fe$_3$O$_4$@([ENR-LDHs] showed a gradual release over time. Under the conditions of pH=4.6 and 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 pH=4.6, the sustained-release equilibrium was reached at 220 minutes, and 85% of ENR was released. At 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 Fe$_3$O$_4$@([ENR-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.

<table>
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<tr>
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<tr>
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<td>[73]</td>
</tr>
<tr>
<td>Fe₃O₄@Zn-Al@Fe-La</td>
<td>Electrostatic action</td>
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<tr>
<td>Fe₃O₄@MgAl-LDHs</td>
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Conclusions

The synthesis and application of novel nano-based materials is rapidly increasing. The advancement in nanotechnology has led to the 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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