Composites of metal-organic frameworks (MOFs) and LDHs for energy storage and environmental applications: Fundamentals, progress, and perspectives

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ABSTRACT

The increasing demand for energy has caused irreversible pollution to the environment. In order to protect the ecological balance, people are constantly exploring materials with excellent energy storage and environmental protection performance. Composites of Metal Organic Frameworks (MOFs) and layered double hydroxides (LDHs) synthesized by MOFs and LDHs has rich electroactive sites, porous structure, high surface area and interactive conductive network, which overcomes the shortcomings of poor conductivity, low electron transmission efficiency and self-accumulation when MOFs and LDHs exist alone, and has attracted the attention of energy storage and environmental protection, and has become a hot material explored by researchers in recent years. In this paper, the applications of the composites of LDHs and MOFs in electrochemical energy storage (EES) and environmental protection in recent years are reviewed. Firstly, the basic characteristics and synthesis route of composite materials are briefly summarized. Secondly, the surface engineering such as heteroatom doping, holes and heterojunction, and the construction of hollow structure and core-shell structure are emphatically introduced. Thirdly, it summarizes its application in energy storage and environmental protection. Finally, the development prospect of composite materials combining LDHs and MOFs is prospected. This review lays a foundation for the development of composite materials of MOFs and LDHs.

1. Introduction

The development of human society is based on the destructive exploitation of the earth’s resources and serious pollution to the ecological environment. Environmental problems such as the consumption of non-renewable energy, the discharge of carbon dioxide and other toxic gases, and the discharge of waste water and waste residue are gradually devouring human living space [1–4]. Based on the above problems, human beings have to develop multifunctional materials with excellent performance for energy storage and environmental protection to cope with the crisis of energy shortage and ecological environment deterioration, etc. [5–7]. Porous functional materials, such as zeolite, porous polymer, activated carbon, metal organic frameworks (MOFs) and layered double hydroxides (LDHs) have been developed by various technologies, designed and applied to energy storage equipment and environmental protection [8–10].

LDHs has a two-dimensional (2D) lamellar structure, which has the advantages of large specific surface area, adjustable gap between layers, exchangeable anions between layers, easy synthesis and low preparation cost. [11–13]. LDHs has been widely used in various environmental protection and energy equipment [14,15]. LDHs with unique 2D layered structure provides a platform for electron transfer chemical species exchange between electrolyte and electrocatalyst, but the stacked layered structure buries a large number of chemical reaction sites, which reduces the reaction activity. In the process of chemical reaction, self-stacking will also occur, which will greatly reduce its electrical conductivity [16].

MOFs is a new type of porous crystal material composed of inorganic metal ions and organic ligands [17,18]. MOFs has adjustable composition, high crystallinity and high specific surface area, which has attracted extensive attention in energy and environmental applications [19–22]. In recent years, MOFs has been widely studied in catalyst, gas storage, adsorption and separation, luminescent materials, batteries, supercapacitors and sensors for its excellent performance [23–27].

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fact, whether MOF is a semiconductor or a molecular entity assembled in a periodic manner is still controversial. The original MOFs has limited charge transfer in the reaction process, which leads to its poor semiconductor properties. At the same time, the moderate strength and wide band gap of the coordination bond between metal nodes and organic ligands make it unsuitable for direct application in the field of photocatalysis [28–30]. In addition, MOFs materials can be used as precursors or sacrificial templates to generate composite materials for various applications, which is regarded as an effective strategy to prepare structurally functional materials [31].

Composites of LDHs and MOFs were synthesized by different synthesis routes. Meanwhile, different preparation methods will introduce heterogeneous interfaces, holes and heteroatoms between LDHs and MOFs to optimize the materials [32]. In the early days, Li designed and directionally grown nano-MOFs on LDHs to synthesize nano-composite materials (MgAl-LDH/MOFs) with high stability and processability, which can be used as a general platform to control thermal decomposition and prepare integrated nano-catalysts [33]. Composites of LDHs and MOFs can inherit the advantages of LDH and MOF and keep their original morphology, which endows them with excellent functional properties, such as extremely high specific surface area, customized porosity, adjustable pore size and diversified composition, making them attractive candidate materials in chemical sensing, gas storage, energy conversion, catalysis and other fields [22,34–36]. In 2018, Zhou synthesized uniform ZIF-67 diamond-shaped dodecahedron penetrating CoMn-LDH nanoneedle array, and then transformed it into shish-kebab type MnCO₂O₄@Co₃O₄ nanoneedle array by thermal annealing in air, as an intermediate, LDHs@MOFs composite not only plays a role in forming a whole, but also can produce synergy or strengthen functions [37].

In recent years, researchers no longer use composites of LDHs and MOFs as an intermediate, but gradually pay attention to the onto logical properties of composites of LDHs and MOFs. In 2019, AsmaKhoobi in situ grew imidazole zeolite skeleton on the surface of layered double hydroxide to prepare porous nanocomposites (Zn-Al LDH/ZIF-8) which were applied to the adsorption extraction and detection of penicillin G (PEN G) [38]. In 2019, Zheng synthesized LDHs nanosheets by hydrothermal method, and then in-situ nucleated on its surface to grow into MOFs nanosheets, after vulcanization, a high conductivity composite (NiAl-LDH/Ni-MOF/S) was obtained [39]. It can be seen that composites of LDHs and MOFs show considerable performance in energy storage and environmental protection, which indicates that it is worthy of our in-depth study in the future. At the same time, we count the published research on composites of LDHs and MOFs in recent eight years in Fig. 1a, and its relative proportion in various applications.

The research of composite materials based on LDHs and MOFs has made great progress, and its application in the fields related to energy and environmental protection is satisfactory. Fig. 1b shows the related research of MOFs@LDHs and LDHs@MOFs composites reported in recent eight years [33,40–60]. With the passage of time, the latest research on the composites of LDHs and MOFs are worth further sorting out and summarizing. However, as far as we know, there is no systematic summary of the achievements. As a valuable kind of composite material, composites of LDHs and MOFs deserves more research. We aim to summarize the research of MOFs@LDHs and LDHs@MOFs composites. Specifically, we introduced the basic characteristics, synthesis methods, structural engineering of composites, its applications in environmental protection such as energy, adsorption and degradation, and advanced characterization technologies. Finally, we discuss the problems faced by this promising MOFs@LDHs and LDHs@MOFs composites in the early stage of development and the possibility in the future.

Fig. 1. (a)Trend chart of papers about composites of LDHs and MOFs published in recent 8 years; (b) The development path of the composites of LDHs and MOFs from the historical point of view.
2. Fundamental characteristics

2.1. LDHs

Layered double hydroxides (LDHs) of two-dimensional hydrotalcite clay are layered structures, and the lamellae are composed of positive charges, and anions are distributed between the lamellae, which are combined with the lamellae through non-covalent interaction [61]. The general formula of LDHs is: \[ \text{M(II)}_{1-x}\text{M(III)}_{x}(\text{OH})_{2}\cdot(x-n)\text{A}^{n-}\cdot y\text{H}_{2}\text{O}. \]

Among them, M(II) is a divalent metal cation; M(III) is a trivalent metal cation; A\(^{n-}\) is an equilibrium anion with an n charge, usually CO\(_3^{2-}\) [13, 62]. Anions and cations keep charge neutrality together, and maintain the overall stability of LDHs [63].

As shown in Fig. 2a, the two-dimensional (2D) layered structure model of LDHs is shown in the established crystal model [64]. M(II) and M(III) of LDHs materials are in the octahedral position in the crystal...
structure [65]. Flexible selection of M(II), M(III) and interlayer anions can control the synthesis of LDHs [66,67]. LDHs have high specific surface area, environmental friendliness, low cost and non-toxicity, and has been widely used as materials for catalysis, drug delivery and environmental remediation. [64,67-69]. Liu et al. prepared ultrathin CoFe-LDH nanosheets (Fig. 2b) [70].

2.2. MOFs

Metal-organic framework (MOF) materials are porous crystalline materials with periodic network structure formed by self-assembly of transition metal ions and organic ligands. [80]. There are several categories of MOF commonly used in the study: isoreticular MOFs (IRMOFs), zeolite-imidazolate frameworks (ZIFs), materials of Institute Lavoisier (MILs), and pocket-channel frameworks (PCNs).

IRMOFs is a repetitive network topology mainly formed by bonding [Zn4O6]4+ metal clusters with carboxylic organic ligands. IRMOFs have large pores and adjustable volume, and carboxylic acid-based organic ligands tend to form clusters with metal ions, thus preventing the penetration of MOFs to some extent. Fig. 2c is a schematic diagram of single crystal X-ray structure of IRMOF-n (n = 1, 2, 3, 4, 5 and 6) [71]. ZIF-8 material is self-assembled by Zn or Co and N on the ring of imidazole (or imidazole derivative) in a four-coordination way. Fig. 2d is a structural diagram of ZIF material [72]. Among ZIFs, ZIF-8 and ZIF-67, which are the Coordination compounds of Zn and Co with -methylimidazole, are common and the most synthesized ones. MILs material is another kind of special MOFs material, which can be coordinated by trivalent transition metal ions (such as Fe, Al and Cr) and carboxylate ligands. MIL-100 (Fig. 2e) [73] is formed by coordinating Fe3+ or Cr3+ with trimellitic acid, while MIL-101 [74] is formed by coordinating transition metal ions with terephthalic acid. In addition, also shows the schematic structure of MIL-124 and MIL-120 [75]. PCNs series materials contain a number of cubic octahedral nano-pore cages, and form a pore cage-channel topology in space. Hong Kong University of Science and Technology-1 (HKUST-1) (Fig. 2f) is a typical PCN, which uses Cu2(COO)4 cluster to coordinate with trimellitic acid, and has two pore structures. One is an orthogonal hole, and the other is a straight three-dimensional orthogonal channel [76].

MOFs has adjustable pore size, multifunctional structure, large specific surface area, multi-metal sites and many other properties. These outstanding characteristics make MOFs used in gas adsorption and storage [80-82], molecular separation [83], sensing [84], catalysis [85,86], drug slow release [87], etc.

2.3. Composites of LDHs and MOFs

In practical application, LDH usually has some defects, such as low conductivity, limited specific surface area, unsatisfactory electro-chemical stability and aggregation tendency [88]. The active site of MOFs material is not easy to approach [89,90], and it is easy to agglomerate in solution, which leads to poor conductivity and stability, resulting in low interfacial reaction kinetics [91,92]. Researchers combined LDHs and MOFs materials to optimize pore size distribution, improve specific surface area, accelerate electron transmission efficiency and participation rate, avoid the problem of conductivity decline caused by long-term electrochemical accumulation of LDHs and MOFs, and break through the performance limitations of a single material. [93,94]. In 2021, Zhang et al. in-situ generated Ni-MOF/LDH heterostructure, which will greatly enhance the electrochemical performance of the materials (Fig. 2g) [77]. In 2020, Soltani et al. designed a layered nanocomposite (LDH/MOF-HNC) based on layered double hydroxide/metal organic framework (Fig. 2h) [78]. The graded three-peak micro-medium-macroporous structure of LDH/MOF-HNC increases the specific surface area of the material. In 2021, Cao et al. prepared functionalized layered double hydroxide/metal organic framework (LDH/MOF) nanocomposites with bimodal micro-mesoporous structure by chemical in-situ method. (Fig. 2i) [79]. The advantages of composites listed above show that the strategy of combining LDHs with MOFs materials has great application potential for energy storage and environmental protection.

3. Routes for the Fabrication

Synthesizing the composites of LDHs and MOFs often requires multiple synthesis steps on the basis of a single material, and all the steps will involve different synthesis methods. At present, the route of synthesizing composites is mainly from two aspects: i) growing MOF materials on LDH, ii) growing LDH materials on MOF.

3.1. Grow MOFs on LDHs

LDHs has adjustable and reasonable interlayer spacing [95]. LDHs scaffold has positive charge and unsaturated metal sites, so it is considered as an ideal template for directional growth of MOFs [41,42,96]. MOFs materials were synthesized on the synthesized LDHs thin films, and the synergistic effect of rapid electron transfer reduced the reversible ion accumulation at the interface and improved the electrochemical activity of composites [40,97].

3.1.1. Hydrothermal method

In a closed pressure vessel, water is used as a solvent, and powder is dissolved and recrystallized to prepare materials. Hydrothermal method is a simple and environment-friendly preparation method, and the samples prepared by hydrothermal method are usually in powder form, with small graininess and difficult agglomeration. Lv et al. prepared the composite material LDHs@MOF-76 for adsorbing U(VI) in aqueous solution by a simple hydrothermal method [98]. Cao et al. used a gas-phase hydrothermal method to grow ZIF-67 on the surface of the EG/CoNi-LDH nanosheet array to obtain a nano-sheet array (EG/CoNi-LDH/ZIF-67) [99]. Similar research was conducted in 2021, when Xu et al. synthesized NiFe-LDH-MOF nanoflowers with three-dimensional gradient by hydrothermal method, and the ratio of Ni/Fe was controllable (Fig. 3a) [100]. Compared with other preparation methods, hydrothermal method is relatively simple and efficient, and is often used in the preparation of nano-materials.

3.1.2. Template method

By depositing other materials on the surface of nano-structured template materials with controllable shapes, and then removing the template materials, nano-materials with standardized template morphology and size can be obtained, which is the template method. In 2020, Cai et al. proposed a template-oriented strategy: to prepare hollow LDH(H-LDH) nanostructures with staggered LDH nanosheets, and then use H-LDH as MOF epitaxial growth template to form hollow MOF capsules [101]. According to this strategy, Cai assembled ZIF-8 onto H-LDH template, and obtained H-LDH@ZIF-8 with hollow structure. (Fig. 3b). The key to synthesize LDHs@MOFs composite with hollow structure is to grow the composite on the base material with hollow structure.

3.1.3. In-situ growth method

In-situ growth method is to use the pretreated carrier surface as a chemical reaction zone, place it in a reaction environment, and simultaneously nucleate and grow on the substrate surface. In 2016, Dou et al. synthesized LDHs thin films on nickel substrate, and then prepared ZIF-67 on it by in-situ growth, and synthesized LDH@ZIF-67 [97]. In 2021, based on bulk FeNi-LDH, Zheng transformed it into corresponding FeNi-MOF by in-situ growth, and obtained 2D/1D FeNi-LDH-MOF nano-hybrid array, which was used as a high-performance OER catalyst (Fig. 3c) [95]. FeNi-LDH nanosheets/MOF are mainly prepared through the following two key processes: i) FeNi LDH is prepared in ultra-thin 2D nanosheets by etching, ii) one-dimensional sword-shaped MOF crystal material is in situ grown on the basis of the previous step. In 2022,
Xu et al. in-situ grew a typical metal-organic framework ZIF-8 on layered double hydroxide, and prepared a new type of composite nano-container (LDH/ZIF-8) [104]. In-situ growth method can avoid the poor compatibility between matrix and functional body, and enhance the tuberculosis between them.

### 3.2. Grow LDHs on MOFs

The introduction of LDHs into MOFs can not only promote the formation of hollow porous structure, but also make the composite have more active sites, and avoid the stacking of LDHs [105]. Composite combines the advantages of single MOFs and LDHs, and is expected to become a material with excellent energy storage and environmental protection.

#### 3.2.1. Chemical etching method

Etching is based on the principle of chemical solution etching, so the machining accuracy is high and the flatness is better. In 2018, Zhao et al. in-situ grew a Co-based MOF polyhedron (ZIF-67) on a hollow carbon nano-cage, and then added Ni(NO$_3$)$_2$ to partially etch ZIF-67 into a Ni-Co layered double hydroxide/hollow carbon nano-cage and nanosheet, forming CNTs@NiCo-LDH/ZIF-67 composite [45]. Zhao et al. synthesized ZIF@LDH core-shell structures based on polystyrene spheres (PSs) template by simple ions, and then converted them into layered double hydroxides (LDH) by chemical etching [90]. In 2022, Zhang et al. used ZIF-67 as the substrate by chemical etching, and etched the surface of ZIF-67 by Ni$^{2+}$ to form Ni$_x$Co-LDH/ZIF-67 composite (Fig. 3d) [102]. By adjusting the concentration of Ni$^{2+}$, the etching rate of MOFs and the growth rate of LDHs can be controlled, so as to achieve the ideal ratio of LDH to MOF.

#### 3.2.2. In-situ pseudocrystal transformation method

On the basis of three-dimensional MOFs template, the original MOFs material is deconstructed by in-situ pseudomorphic transformation, and the dispersed metal and organic anions participate in the growth of LDHs in order, which will form a uniformly extended MOFs@LDHs [31,96]. In 2020, Huo et al. developed a general strategy: in-situ pseudomorphic transformation, and in-situ grown ultra-thin FeNi-LDH nanosheets in heterogeneous MOF to construct MOFs@LDHs electrocatalysts (Fig. 3e) [89]. The layered Fe-Ni LDH/MOFs prepared in this study has excellent electrochemical activity, which is closely related to the rich active sites on the surface of the composite and the electron transport channels created by inserting LDHs arrays. Many MOFs are completely transformed into LDH structure under the condition of organic ligand decomposition of organic ligands, Which can not retain the original morphology structure and advantages. In-situ pseudomorphic transformation can effectively epitaxially transform the precise and controllable part of MOF template to prepare mixed MOFs@LDHs composites.

#### 3.2.3. Electrodeposition method

Electrodeposition is a process of forming a deposit on the solid surface by oxidation reaction on the anode of electrolytic cell or ion reduction reaction and electrocrystallization on the cathode under external power supply. At present, it is common to study the application of electrodeposition in the synthesis of MOFs@LDHs composites. For example, in 2022, Liu et al. synthesized CoMn LDHs on Co-HKUST substrate by electrodeposition, forming a new core-shell structure Co-HKUST@CoMn-LDHs composites [94]; Zhang et al. synthesized HKUST-1@CoNi LDHs by electrodeposition [106]. Similarly, in 2022, Zeng et al. synthesized the Ni-Fe layered double hydroxide @ Ni metal-organic framework /Ni foam (NiFe-LDH@Ni-MOF/NF) heterostructure
by electrodeposition (Fig. 3f) [103]. The hierarchical structure of NiFe-LDH and Ni-MOF promoted the edge defects of the composite and exposed more active sites, resulting in higher catalytic activity.

3.3. Summary

Previous studies have shown that it is completely feasible to prepare composites by growing MOFs on LDHs substrate, or to grow LDHs on MOFs substrate to form composites. At the same time, the structure of the base material largely determines the structure of the composites, which provides ideas for preparing composites with different structures. The above mentioned hydrothermal method, sublimation-vapor pseudocrystal transformation, template strategy and in-situ strategy are all effective methods to prepare composites. In addition, the advantages and disadvantages of various methods for synthesizing composites of LDHs and MOFs are summarized in detail in Table 1, which provides reference information for synthesizing composites.

4. Optimization strategy

4.1. Modification strategy

A defect in a crystal structure that deviates from the normal arrangement of the crystal structure at or within the adjacent microscopic region of a junction is called a point defect, also known as a zero-dimensional defect. Point defects occur in one or several lattice constants in crystals, and there are three types: vacancy, interstitial atom and impurity atom. By creating defects, the electrical conductivity of semiconductor materials and the luminescence of light-emitting materials can be increased [107]. In addition, the formation of homotypic heterojunctions (p-p or n-n) or heterotypic (p-n or n-p) heterojunctions in the transition region where the two conducting materials are in contact will add to promote electron transport. Therefore, introducing vacancy, heteroatom doping and heterostructure into composites can increase its active sites and improve its properties.

4.1.1. Vacancy creation

Due to the fluctuation of energy, some atoms with high energy will overcome the constraints of the surrounding atoms and migrate to other places, leaving vacancies in the original equilibrium position. Oxygen vacancy is the most commonly used and studied defect type [108], have been widely introduced into two-dimensional nanostructures to accelerate the kinetics of surface redox, which exhibit enhanced performance in terms of energy storage and catalytic capacity [109,110]. In 2019, Chen et al. developed a 3D porous nanostructure NiCo-LDH@ZIF-67-Vo/NF [111]. The surface of ZIF-67 was decorated with NiCo-LDHs, and rich oxygen vacancies (VO) were etched (Fig. 4a) [112,113]. Due to the synergistic between oxygen vacancies and LDH nanosheets, Ni-based LDH@ZIF-67-Vo/NF catalysts show higher specific surface area and abundant active sites. Therefore, NiCo-LDH@ZIF-67-Vo/NF nanostructures can provide easy mass diffusion and rapid charge transfer, thus significantly increasing the catalytic active sites [83,114,115]. It is worth noting that the optimized NiCo-LDH@ZIF-67-Vo/NF electrode material shows excellent OER performance under alkaline conditions. In 2020, Wu et al. prepared porous NiFe-LDH nanosheets (NiFe-LDH/ZIF-67) induced by ZIF-67 [116]. X-ray photoelectron spectroscopy analysis showed that NiFe-LDH/ZIF-67 contained more oxygen vacancies than the original NiFe-LDH and had higher electrocatalytic activity.

Different from the traditional modification from morphology, size and composition, vacancy engineering provides a new idea for the development of high-efficiency energy conversion of non-precious metal electrocatalysts.

4.1.2. Heteroatoms doping

Impurity doping is a promising strategy to control electronic structure, which can improve the cycle stability and activity of electrocatalysts. In addition, the introduction of heteroatom doping into the material can adjust the electron density and rearrange electrons to improve the charge transfer ability and electrocatalytic performance of the material [117]. In 2016, Shang et al. constructed Mo-doped CoNi MOFs@LDHs nanosheets loaded on Ni foam (Fig. 4b) [57]. Thanks to its unique structure, MOF@LDH-Mo shows unprecedented intrinsic activity to benzylamine oxidation reaction (BOR), and can be used as an electrocatalyst for BOR, instead of OER to promote hydrogen evolution. This study provides an environment-friendly water-based electrocatalysis way for the production of valuable chemicals and green energy hydrogen.

The doping of metal into LDHs@MOFs composite material changes the electronic structure of nano-materials, effectively reduces the energy barrier, increases the density of reaction sites, forms a synergistic effect with the original metal, ensures high conductivity, and realizes excellent electrocatalytic performance [118].

4.1.3. Heterojunction

Type II heterojunctions [119], p-n heterojunctions [120], S-scheme heterojunctions [121], and Z-scheme heterojunctions [122] are all widely recognized heterostructure techniques and also a reasonable way to prepare efficient catalysts. Introducing heterojunction between LDHs and MOFs is a common surface modification method. The regular and precise lattice arrangement of MOFs makes it possible to quasicrystal grow LDHs materials on MOFs materials, and heterostructures will also be formed at the interface between the two materials. In 2021, Wang et al. designed a novel multi-layer porous cMOF/LDH heterogeneous nanotube array (Fig. 4c) [32]. Combining the advantages of 2D cMOF and LDH, the cMOF/LDH-48 heterojunction nanotube array has a rich porous structure, which increases the specific surface area of the composite and increases the surface electroactive sites, thus achieving high conductivity. In 2021, CoAl-LDH@Ni-MOF-74 prepared by Jin has S-scheme heterojunction, showing higher photocatalytic hydrogen evolution activity [123]. In 2022, Wang et al. designed a monodisperse ruthenium (Ru) site coupled cMOF/LDH heterogeneous nanotree array catalyst (cMOF/CoNiRu-NT) (Fig. 4d and e) [124]. The composite material has a uniform, vertically growing, tree-shaped conical heterostructure, and produces more vacancies, providing more free electrons at the heterojunction, showing extraordinary overall water decomposition activity and catalytic stability in alkaline medium. In 2022, Huang et al. constructed MIL-101@OX- metal organic framework (MOF) by

Table 1

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
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<tbody>
<tr>
<td>Hydrothermal</td>
<td>The product has uniform appearance, good crystallization and good dispersion.</td>
<td>The equipment requirements are high, the safety performance is poor, and the mother liquor of products is different.</td>
</tr>
<tr>
<td>Template</td>
<td>The device is simple, the operating conditions are mild, and the morphology and structure of the material can be accurately controlled.</td>
<td>Uniform pore size of materials, sacrificing of templates, and difficulty in scale preparation.</td>
</tr>
<tr>
<td>In-situ growth</td>
<td>Small particles, stable performance and easy operation.</td>
<td>Poor material dispersion, hole blockage and other shortcomings.</td>
</tr>
<tr>
<td>Chemical etching</td>
<td>No pollution, convenient operation.</td>
<td>Cannot batch.</td>
</tr>
<tr>
<td>In-situ pseudocrystal transformation Electrodeposition</td>
<td>Uniform product and controllable thickness.</td>
<td>The reaction process is out of control. The rate of nucleation and growth of crystal nuclei on the substrate can not be controlled.</td>
</tr>
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</table>
"MOF on MOF" method, and then transformed it into MIL-101@NiFe layered double hydroxide (LDH) in alkaline solution [125]. The heterostructure composite prepared by this unique preparation method optimizes the phase interface, and provides new insights for electrochemical catalysis and other fields. By designing and synthesizing heterostructures when synthesizing materials, the transport of electrons and ions can be effectively promoted, thus improving the electrochemical properties of materials [32]. MOFs@LDHs and LDHs@MOFs composites have excellent properties due to the introduction of heterojunction, and are often used in the fields of transistors, light emitting components, OER, SCs, etc.

4.2. Structure construction

As we all know, performance is closely related to the structure of matter. Composites of LDHs and MOFs are often prepared into hollow or core-shell structures in current research. [89,127,128] In the research, it is a common way to improve the structure of nano-materials by preparing them into hollow structures or core-shell structures.

4.2.1. Hollow structure

The material with hollow structure has two surfaces, inner and outer, so its specific surface area will be greatly increased, and a large number

![Figure 4](image-url)
of active sites and rich active edges will be obtained, which will provide a good platform for the deposition of other components [129,130]. The material with hollow structure will have good electronic conductivity, and at the same time, the hollow structure will effectively reduce the structural strain caused by repeated insertion/extraction process, prevent the agglomeration of nanoparticles and adapt to the volume change in the electrochemical reaction process [131,132]. In 2020, Huo et al. prepared the mixed LDH/MOF material (Fe–Ni LDH/MOF-B2) with hollow structure by precisely controllable partial epitaxial transformation of MOF template [89]. In 2021, Huang et al. removed the ligand in Co-MOFs by chemical etching strategy, and produced ultra-thin amorphous CoFe LDH nanosheets, thus obtaining a one-dimensional nanorod array composed of carbon fiber cloth-supported CoFe layered double hydroxide (LDH)/metal organic framework (MOF) (Fig. 4f) [55].

In the above examples, the researchers synthesized hollow LDHs@MOFs materials by template method and chemical etching method. Hollow composites of LDHs and MOFs also have the advantages of low mass density, excellent electrochemical performance and large specific surface area due to their hollow structure, and gradually become potential candidates in the fields of catalysis and energy [133].

4.2.2. Core-shell structure

Nanomaterials with core-shell structure are the research hotspots in recent years [134]. Core-shell materials have attracted more and more attention because of their outstanding properties [135,136]. (i) Multifunctional: combining the properties of core and outer core materials of core-shell nanomaterials will expand the application of core-shell materials in electronics, optics, magnetism and catalysis [137]. (ii) Adjustability: by changing the size, shape, morphology and composition of core and shell, the properties of core-shell nanomaterials can be easily adjusted. [138]. (iii) Stable core dispersibility: the shell structure as the support of the core-shell structure protects the inner nanoparticles from aggregation, sintering or other agents [139]. (iv) Controllability: It is very important for drug application to master the controllability of core release of core-shell structure materials for drug transportation, and this goal can often be achieved by changing the pH and temperature of solution environment [140]. Chen et al. synthesized ZIF-67@Co-LDH yolk–shell heterostructure (Fig. 4g) [50]. In ZIF-67@Co-LDH egg core-shell structure, the Co-LDH shell material not only serves as a protective shell to fix the core ZIF-67 material in the inner core, but also serves as a channel for electrons/charges to shuttle freely between the inner core and the external environment. ZIF-67@Co-LDH yolk shell ball shows high loading and slow release rate of rhodamine molecules, which is used in the fields of sustained-release capsules. In 2020, Li et al. deposited ZIF-67 on Co-LDH, and designed a novel core-shell heterostructure of Co-LDH@ZIF-67 (Fig. 4h), which enhanced the catalytic activity and stability of the material [126]. ZIF-67 and Co-LDH, as the inner core and outer core of the core-shell structure of Co-LDH@ZIF-67, have heterogeneous structures at the interface, and the large specific surface area and porous structure bring electrochemical activity and long-term stability to the materials.

The unique structure of core-shell composites can achieve fascinating properties, but it is difficult to further optimize it systematically. The special structure of core-shell MOFs@LDHs composite makes it an irreplaceable superior material in the fields of drug delivery and release, catalysis, electric storage and so on.

4.3. Summary

In the above two sections, we elaborate the optimization strategy of composites from two aspects: surface modification and structure construction. Surface modification focuses on optimizing materials on the surface of crystal structure, while structure construction focuses on preparing advantageous structures. However, the strategy of MOFs@LDHs and LDHs@MOFs composites still has more room for development. We summarize it in the following points:

(i) Oxygen vacancy is the most common vacancy modification type. In the future research, we should explore more vacancy types and enrich the application of vacancy modification system in composites of LDHs and MOFs.

(ii) Metal heteroatom doping is a widely used doping type. In the future research, we should encourage more types of metal atom doping and even nonmetal element doping to be applied to the research of composites.

(iii) The properties of composites will be improved to a higher level by introducing other optimization strategies on the basis of preparing them into heterostructures.

(iv) At present, composites of LDHs and MOFs are often prepared into hollow and core-shell structures, and more advantageous structures should be developed in future research.

5. Energy storage applications

The rapid development of human society depends on a huge demand for energy [141,142]. However, the energy shortage caused by the continuous consumption of non-renewable energy sources will severely limit human development [143,144]. Human beings have tried to store energy by developing new electrochemical energy storage (EES) devices with excellent durability [145–147]. Among the current energy storage systems, electrochemical energy storage has become the most ideal energy storage system because of its sustainable environmental characteristics, high conversion rate and abundant reserves [148,149]. The EES device is mainly composed of two parts: the battery and the supercapacitor. There is a big contrast between batteries and supercapacitors in performance. Compared with supercapacitors, batteries often have higher energy density, but in terms of power density, the performance of batteries is far less than that of supercapacitors. [150,151]. The battery stores charge with a large specific capacity, and a large number of ions are often embedded in the electrode material, so the battery can obtain high energy density [152,153]. The high power density of supercapacitors is due to the fact that no charge transfer kinetic limitations such as redox reactions are involved [154]. With the rapid development of society, batteries are required to have ultra-high performance beyond their current capabilities: energy and power density must be close to theoretical limits, and excellent life and reliability, as well as enhanced safety and environmental sustainability must be achieved [155,156]. Asymmetric supercapacitor (ASC) is considered as the next generation advanced supercapacitor, with increased battery voltage of high energy and power density [157]. The electrochemical properties of EES devices are mainly due to the electrode materials [158]. Therefore, it is an important way to enrich the field of electrochemical storage to develop materials with higher electrochemical properties as electrode materials and catalytic conversion energy materials [159,160]. Fig. 5 shows the schematic diagram of lithium-sulfur battery, zinc-air battery and supercapacitor. The applications of MOFs@LDHs and LDHs@MOFs composites in batteries and supercapacitors are summarized in Table 2.

5.1. Lithium-sulfur battery

Lithium-sulfur battery is a kind of lithium battery, which uses lithium as the negative electrode and sulfur as the positive electrode. The advantages of lithium-sulfur battery are that its maximum specific capacity can reach 1675 mAh g⁻¹, and its energy density can reach 2600 Wh kg⁻¹ at the same time, the sulfur cost required for preparing lithium-sulfur battery is low, which makes it a promising energy storage device [161]. The excellent performance of LSBs enables it to meet the rapidly growing energy demand, and the irreplaceable advantages of LSBs make it have the potential to surpass LIBs in practical application. The energy of LSBs comes from the electrochemical redox reaction.
between lithium sulfide and sulfur, and a series of intermediate polysulfides will be produced in the electrolyte during the reaction \[ 162 \]. The commercialization of Li-S battery is hindered by poor conductivity of sulfur, shuttle effect and slow reaction kinetics \[ 163 \].

5.1.1. Application

MOFs materials are efficient sulfur adsorbents and reaction accelerators \[ 164,165 \]. There are often abundant hydrophilic adsorption sites on the surface of LDHs materials. In the lithium-sulfur battery system, the combination of lithium polysulfide (LiPSs) and these
hydrophilic adsorption sites can achieve a better electron/ion transport process [166, 167]. Zhang et al. designed a new type of MgCo-LDH/ZIF-67 composite with yolk-shell structure was prepared on the basis of ZIF-67 particles. Adding MgCo-LDH/ZIF-67 composite with yolk-shell structure as the cathode of Mg battery, has an ultra-high specific capacity of 1187 mAh g⁻¹ at 0.1 C and a high specific capacity of 633 mAh g⁻¹ after 1000 cycles at 1C (Fig. 6h, 6i). In the Li₂S nucleation experiment, the Li₂S precipitation capacity/peak current of the battery with NiCo–MOF/LDH is 234.7 mAh g⁻¹/0.162mA, which is higher than that of the batteries with NiCo–MOF and NiCo–MOF/LDH, which are 186.5 mAh g⁻¹/0.154mA and 123.9 mAh g⁻¹/0.151mA respectively (Fig. 6j-l). All these results show that NiCo–MOF/LDH has the strongest promoting effect on the transformation of LiPSs. The calculation shows that the NiCo–MOF/LDH interlayer inhibits the shuttle effect and polarization effect (Fig. 6m). Specifically, the tightly packed NiCo–MOF/LDH can physically block and chemically adsorb LiS, thus effectively confining LiS to the cathode side. In addition, NiCo–MOF nanorods catalyze the transformation of adsorbed LiPSs to reduce polarization effect and improve the utilization rate of active substances. Therefore, with NiCo–MOF/LDH interlayer, the rate performance and cycle stability of Li-S battery are better than those of similar batteries in this study [168]. As the electrode material or sandwich material of lithium-sulfur battery, composites of LDHs and MOFs show that the synergistic effect between LDHs and MOFs is helpful to the battery performance.

### 5.1.2. Mechanism

Simply put, the redox reaction between metals Li and S₈ constitutes the basic working principle of lithium-sulfur battery [173].

**Anodic reaction:** \( Li \leftrightarrow Li^+ + e^- \)  
**Cathode reaction:** \( S_8 + 16Li^+ + 16e^- \rightarrow 8Li_2S \)

During the LSB discharge, the cathode sulfur gradually reduces to polysulfide (Li₂Sn, 4 ≤ n ≤ 8) and low-order sulfide (Li₂S and Li₂S₂) [174].

\[ S_8 + 2Li \rightarrow Li_2S_8 \]  
\[ Li_2S_n + 2Li \rightarrow Li_2S_{n-2} + LiS_n \]  
\[ Li_2S_n + 2Li \rightarrow Li_2S_{n-2} + LiS_n \]  
\[ Li_2S_n + 2Li \rightarrow Li_2S_{n-2} + LiS_n \]

This process can be expressed as the reaction sequence of \( S_8 \rightarrow Li_{2n-4} \rightarrow LiS_2/Li_2S. LiS_2 \) will also be transformed into Li₂S, but this process is extremely slow and there is serious polarization.

\[ Li_2S_n + 2Li \rightarrow Li_2S \]  

### Table 2

Application examples of compound of LDHs and MOFs in batteries and SCs.

<table>
<thead>
<tr>
<th>Nano-structures</th>
<th>Application</th>
<th>Electrolyte</th>
<th>Voltage windows</th>
<th>Specific capacitance (current/scan rate)</th>
<th>Cycling stability (cycles, current density)</th>
<th>Energy density max</th>
<th>Power density max</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-MgCo-LDH/ZIF-67</td>
<td>LSB</td>
<td>—</td>
<td>—</td>
<td>1121 mAh g⁻¹ (0.2C) 99.95% (500, 1,000)</td>
<td>1147 mAh g⁻¹ (0.1C) 99.3% (1000, 1C)</td>
<td>—</td>
<td>—</td>
<td>127</td>
</tr>
<tr>
<td>NiCo-MOF/LDH</td>
<td>LSB</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Ni-MOF/LDH</td>
<td>ZABs</td>
<td>0.2M ZnCl₂+6M LOH</td>
<td>0.1-0.2 V (vs. Hg/HgO)</td>
<td>342 mAh g⁻¹ (1.5 A g⁻¹)</td>
<td>54% (5000, 2.5 mA cm⁻²)</td>
<td>572.5 W h kg⁻¹</td>
<td>62.81 W g⁻¹</td>
<td>168</td>
</tr>
<tr>
<td>SCNF-@Ni@MOF@NiCo LDH/Zn</td>
<td>ZBNs</td>
<td>6M KOH+0.2 M Zn (CH₃COO)₂</td>
<td>1.4V-2V</td>
<td>71.3 F g⁻¹ (1 A g⁻¹)</td>
<td>100.53 C g⁻¹</td>
<td>81.4% (5000, 10 A g⁻¹)</td>
<td>42.3 W h kg⁻¹</td>
<td>170</td>
</tr>
<tr>
<td>ZIF-9@CoAl LDHs//AC</td>
<td>SC</td>
<td>6 M KOH</td>
<td>0.0-0.5 V (vs. Ag/AgCl)</td>
<td>167.5 F g⁻¹ (10 A g⁻¹)</td>
<td>74.0% (5000, 10 A g⁻¹)</td>
<td>71.9 W kg⁻¹</td>
<td>—</td>
<td>171</td>
</tr>
<tr>
<td>NiV LDH@ZIF-67//AC</td>
<td>SC</td>
<td>6 M KOH</td>
<td>0.0-0.6 V (vs. Ag/AgCl)</td>
<td>100.53 C g⁻¹ (10 A g⁻¹)</td>
<td>74.0% (5000, 10 A g⁻¹)</td>
<td>25.7 W h kg⁻¹</td>
<td>—</td>
<td>172</td>
</tr>
<tr>
<td>Co-HKUST1@CoMn-LDHs//AC</td>
<td>SC</td>
<td>6 M KOH</td>
<td>0.0-0.5 V (vs. SCE)</td>
<td>194.0 F g⁻¹ (2 A g⁻¹)</td>
<td>90.0% (5000, 10 A g⁻¹)</td>
<td>39.8 W h kg⁻¹</td>
<td>199.9 W kg⁻¹</td>
<td>106</td>
</tr>
<tr>
<td>NiCo-LDH@MOF//AC</td>
<td>SC</td>
<td>—</td>
<td>0.0-0.6 V (vs Hg/HgO)</td>
<td>—</td>
<td>39.8 W h kg⁻¹</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>HKUST1, @CoNLDH//AC</td>
<td>HSC</td>
<td>6 M KOH</td>
<td>0.0-0.6 V (vs Hg/HgO)</td>
<td>256.0 F g⁻¹ (1 A g⁻¹)</td>
<td>91.0% (5000, 3 A g⁻¹)</td>
<td>184 W h kg⁻¹</td>
<td>1291.0 W kg⁻¹</td>
<td>58</td>
</tr>
<tr>
<td>ZIF-8/Ni/CoLi(50%)/ZIF-382/ ZnLDH//AC</td>
<td>SC</td>
<td>6 M KOH</td>
<td>0.1-0.5 V (vs. SCE)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>
5.3. Ni-Zn battery

Nickel-zinc batteries (NZBs) consist of nickel cathode, zinc cathode, diaphragm and electrolyte. NZBs have excellent high-speed discharge capability, high capacity, higher nominal voltage, low cost, safety and reliability, which makes NZBs have a greater application prospect in the field of backup power, emergency power and portable electronics. However, the market outlook for nickel-zinc batteries is not optimistic. As a traditional battery technology, the share of NZBs in the current market has been replaced by new technologies such as lithium-ion batteries (LIBs). The main reason for this situation is the shortcomings of the electrodes of NZBs. The zinc negative electrode of NZBs is subject to zinc dissolution, corrosion, shape change and dendrite growth, and the nickel positive electrode is subject to degradation during charge and discharge [182]. Fortunately, studies have been conducted to effectively improve the zinc cathode dendrite formation and other problems, effectively improving the cycle stability performance of NZBs [183,184]. With the increasing demand for a new generation of portable electronics, the pursuit of better performance of NZBs will be a future research goal.

5.3.1. Application

The electrode electrochemical performance largely determines the performance of the whole battery. LDHs composition is easy to adjust, the structure is easy to tailor and easy to compound with other materials for functionalization, and MOFs have porous structure, excellent specific surface area and multifunctionality, both of which will provide the opportunity to solve the shortcomings of Ni-Zn batteries such as low energy density and poor functional density. In 2023, Xia et al. designed and prepared SCNF@Ni@MOF@NiCo LDHs yarn electrodes with triangular micron sheet arrays and nanosheet structures on silver-plated nylon fibers (SCNF) by an etching-deposition-growth process (Fig. 6p). The triangular macro-nanosheet hierarchy of the yarn electrode is in point contact with the yarn, and thus, the electrode can be bent, twisted and compressed (Fig. 6s). It is applied to the cathode material of one-dimensional filamentary Ni-Zn batteries, which has high specific surface area and ultra-high structural stability even when the yarn is bent. Meanwhile, the abundant active sites of the cathode, good electron conduction and fast ion diffusion bring excellent performance to the Ni-Zn battery. The assembled aqueous Ni-Zn cells have suitable capacitance...
(342 mAh g\(^{-1}\) at 7.6 A g\(^{-1}\)) (Fig. 6q), suitable energy density (572.5 Wh g\(^{-1}\) at 2.59 W g\(^{-1}\)) and excellent stability (55% after 5000 cycles) (Fig. 6r). The excellent flexibility and high capacity retention of Ni-Zn batteries in this study demonstrate their great potential for application in wearable energy storage devices [169].

5.3.2. Mechanism
A simple schematic of a Ni-Zn cell is shown in Fig. 6s. In the discharged state, the cell is connected to an external load and the zinc electrode oxidizes and dissolves into the electrolyte in the form of zincate (Zn(OH)\(_4\)) ions. The intermediate reactions are concentrated near the electrode surface. Once the zincate ion is supersaturated in the electrolyte, the flowing zincate ion will form a zinc oxide precipitate. Electrons are released via the collector through the load and reach the cathode, i.e., hydroxyl nickel oxide [185,186]. The reversible anodic reactions are summarized in Eqs. (1) and (2):

\[
\text{Zn} + 4\text{OH}^- \leftrightarrow \text{ZnO} + 2\text{H}_2\text{O} + 2\text{e}^- \tag{11}
\]

\[
\text{Zn(OH)}_2^{2-} \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2\text{OH}^- \tag{12}
\]

Hydroxy nickel oxide is reduced and hydroxide is formed after receiving electrons from the anode [187]. The reversible cathodic reactions are summarized in Eq. (3):

\[
2\text{NiOOH} + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{Ni(OH)}_2 + 2\text{OH}^- \tag{13}
\]

Equation (4) summarizes the overall reversible reactions of the NZBs system:

\[
2\text{NiOOH} + \text{Zn} + 2\text{H}_2\text{O} \leftrightarrow 2\text{Ni(OH)}_2 + \text{ZnO} \tag{14}
\]

5.3.3. Summary
Finding suitable advanced electrode materials by improving the problems of dissolution and dendrite growth that can occur in zinc cathodes and the degradation of nickel cathodes is the main way to improve the performance of Ni-Zn batteries. The synergistic effect between both LDHs and MOFs has made a great contribution to the improvement of Ni-Zn battery performance. We expect the application of composite materials of LDHs and MOFs in Ni-Zn battery electrodes will be more intensive in the future serious.

5.4. SCs
Supercapacitor is recognized as a high-efficiency electrochemical energy storage device at present, because it has the advantages of fast charge-discharge time, capacitive performance and cycle stability [188]. However, SCs has a low energy density and can only be used as a secondary power supply in practical applications. Therefore, it is the future research direction to improve the potential and diversity of supercapacitors by increasing their high energy and power density [189]. MOFs and LDHs materials are ideal electrode materials for supercapacitors [93,190–192], but its application is limited by its low conductivity [193,194]. MOFs and LDHs form a composite material, and the unique structure can increase the contact area required for electrochemical reaction, which is beneficial to the mass transfer of electrolyte, thus improving Faraday oxidation-reduction reaction [93].

5.4.1. Application
Improving conductivity and constructing specific nanostructures are two effective methods to improve the charge storage of LDH-based electrode materials.

Wang introduced 2D ZIF-9 micro-chip on CoAl LDHs to improve the conductivity [170]. In the same year, Wang also synthesized NiV LDH@ZIF-67 p-n heterojunction by “boat in bottle” method. The asymmetric carbon supercapacitor assembled from NiV LDH@ZIF-67 composite showed a high energy density of 42.3 W h kg\(^{-1}\) at a power density of 520.6 W kg\(^{-1}\) and a 120% energy storage rate (81.4% of NiV LDH//AC) after 5000 cycles [171].

Core-shell structure is also a unique structure, which can integrate the properties of internal and external materials and complement each other’s shortcomings. Liu et al. prepared composite electrode materials (Co-HKUST@CoMn-LDHs) with core-shell structure by combining hydrothermal method and electrodeposition method (Fig. 7a) [94]. The synergistic effect between the inner and outer cores of the composite material makes the electron transmission and participation rate higher. Co-HKUST@CoMn-LDHs composites have excellent properties. Through the test, the specific capacity of 1008.8 F g\(^{-1}\) can be obtained at the current density of 1 A g\(^{-1}\), and the capacity retention rate is 79.6% after 1000 cycles at 5 A g\(^{-1}\) (Fig. 7b, 7c). At the same time, Co-HKUST@CoMn-LDHs composite and activated carbon were assembled into an asymmetric supercapacitor device, which showed a high specific capacitance of 313.8 F g\(^{-1}\), and the corresponding energy density could reach 90.2 W kg\(^{-1}\) at a power density of 719.0 W kg\(^{-1}\) (Fig. 7d, 7e).

The particularity of structure will have a great influence on the properties of materials. Shi et al. tried to synthesize a kind of material with special structure, which is a nano-sheet (NiCo-LDH/MOF) with three-dimensional interconnection hybridization. The manufacturing process is simply by transforming ZIF-67 into NiCo-LDH nano-sheet and anchoring it on the surface of 2D NiCo-MOF (Fig. 7f) [172]. NiCo-LDH@MOF hybrid nanosheets have excellent properties, and the test shows that their specific capacity can reach 723 C g\(^{-1}\) at 1 A g\(^{-1}\) (Fig. 7g). In addition, when they are used as electrode materials for asymmetric supercapacitors, they will still maintain the energy density of 40.26 W h kg\(^{-1}\) at the functional density of 850 W kg\(^{-1}\) (Fig. 7h).

Multi-metal LDHs can show strong electron coupling and fast charge transfer [195]. The construction of multi-metal LDHs with controllable porous morphology is of great significance for improving electrochemical performance and durability [196–198]. In 2022, Zhang et al. controllably constructed the ion diffusion enhancement interface of HKUST-1@CoNi-LDH by in-situ electrodeposition process (Fig. 7i) [106]. HKUST-1@CoNi-LDH composite has excellent properties because of its own multi-metal synergistic effect, and its specific capacitance can reach 2377.8 F g\(^{-1}\) at 1 A g\(^{-1}\) (Fig. 7j). A maintained high Cs of 1688.9 F g\(^{-1}\) at 10 A g\(^{-1}\) for HKUST-1@CoNiLDH (Fig. 7k). The composite material and activated carbon were assembled into HSC (Fig. 7l), HKUST-1@CoNi-LDH//AC showed a high energy density of 39.8 W h kg\(^{-1}\) at a power density of 799.9 W kg\(^{-1}\) (Fig. 7m), and after 5,000 cycles, it had an excellent charge-discharge cycle of 90% capacitance retention rate (Fig. 7n).

Adjusting the ratio of metal ions in LDHs will contribute positively to the electrochemical performance of supercapacitors. In 2022, Hajargasht et al. adjusted the percentage of Ni and Co in LDHs, and ZIF-8/Ni (17%Co(50%)(Al_(33%))LDH showed excellent specific capacitance [58]. The specific capacity, energy density and cycle stability of the asymmetric supercapacitor have good performance. What can be found in this study is that different proportions of elements lead to different interaction effects, which has great influence on the performance of electrode materials.

5.4.2. Summary
By adjusting the interface, nano-structure, metal element types and different proportions between MOFs and LDHs, the shortcomings of poor hydroxide aggregation and conductivity of LDHs and poor conductivity of MOF can be effectively avoided, and the performance of supercapacitors can be enhanced.

6. Environment applications
Removal of toxic pollutants from wastewater by porous adsorbents is considered to be one of the most promising water purification methods. The composite material of MOFs and LDHs is a promising adsorption material for removing harmful pollutants from source water [199]. In addition, the excellent photocatalytic properties of composites can
Sustainable Materials and Technologies 37 (2023) e00691

14


degrade pollutants in water. All the researches related to the application of MOFs@LDHs and LDHs@MOFs composites to environmental protection involved in this section are listed in Table 3.

6.1. Adsorption

6.1.1. Heavy metals

Water pollution is the cause of widespread public health problems. Heavy metals released by human activities, such as leather, cosmetics, electronic products and battery manufacturing, are one of the main

Fig. 7. (a) Synthesis diagram of Co-HKUST@CoMn-LDHs, (b) the GCD curves of Co-HKUST@CoMn-LDHs at different current densities, (c) the EIS analysis of Co-HKUST, CoMn-LDHs and Co-HKUST@CoMn-LDHs, (d) GCD curves at different current densities, (e) the cycle performance at 10 A g\(^{-1}\) of Co-HKUST@CoMn-LDHs//AC asymmetric supercapacitor [94]. Copyright 2022, Elsevier. (f) Schematic illustration of synthesis process of NiCo-LDH@MOF hybrid nanosheets, (g) the specific capacity at different current densities, (h) Ragone plots of NiCo-LDH@MOF//AC and NiCo-LDH//AC [172]. Copyright 2022, Elsevier. (i) Schematic illustration of the synthesis process, (j) GCD curves at a current density of 1 A g\(^{-1}\), (k) specific capacities at various current densities, (l) Schematic diagram of HKUST-1@CoNiLDH//AC HSC, (m) Ragone plot comparison with reported LDH-based SCs, (n) cycling stability at a current density 10 A g\(^{-1}\) for the HKUST-1@CoNiLDH//AC HSC device [106]. Copyright 2022, Springer.
reasons for the deterioration of environmental pollution [200]. In 2019, Wang et al. synthesized carbon fiber/Co-Al layered double hydroxide/zeolite imidazole skeleton-8(CF/LDH/ZIF-8) composites, and used them to efficiently remove toxic metal ion chromium from aqueous solution (Fig. 8a) [201]. When the molar ratio of Al3+/Co2+ reaches 2:3, the specific surface area of the nanocomposites is as high as 156.9 m².g⁻¹ (Fig. 8b), and the pore size distribution is almost within the narrow range of 2.5-8.3 nm (Fig. 8c). In the presence of CF/LDH/ZIF-8 composite material in the solution, the toxic chromium Cr(VI) can be quickly removed, the removal rate is close to 99.3% (Fig. 8d), and it shows excellent cycle stability. In the research of Ghahremani in 2022, they devoted themselves to applying the prepared LDH@MOF-76 complex to remove the highly toxic elements thallium (Tl) [79, 202], Cd(II), Pb(II) [203], and successfully real-

6.1.2. Halogen elements

The water pollution caused by halogen element is a problem that cannot be underestimated. As a halogen element, bromine has high added value in reagent application. Bromine is an important chemical raw material in the chemical production process, so the demand for bromine is very large [214,215]. Traditional bromine extraction methods, including solvent extraction, ion exchange [216], membrane separation [217] and adsorption [218], on the basis of predecessors’ efforts, we are committed to improving the problems of secondary pollution, high input cost and low efficiency existing in traditional methods, and have achieved some results at present. In 2022, Jiang et al. prepared Ni-MOF(D)/NiCo-LDH thin films for effectively removing bromine ions from water, (Fig. 8e and 8f) [204], and successfully realized the extraction of Br⁻ in ESIX system, and the extraction capacity was as high as 126.30 mg g⁻¹ (Fig. 8g and 8h). Iodine isotope is a kind of hard radionuclide [219]. Meanwhile, iodine and its compounds are widely used in many fields, such as agriculture and medicine [220]. In 2020, Yu et al. used CuBi–CO₂–LDH as a general platform, and synthesized three-dimensional layered flower-like ZIF-67/CuBi–CO₂–LDH composites by simple coprecipitation method. Good iodine adsorption performance shows that ZIF-67/CuBi–CO₂–LDH is a promising adsorbent in the field of iodine capture [54]. The release of halogen elements will cause ecological pollution in the environment, and the collection and fixation of halogen will create more value.

6.1.3. Organic pollutants

The discharge of highly toxic anionic organic dyes in industrial wastewater has caused great harm to the whole ecosystem. It is an appropriate treatment method to apply MOFs/LDHs composite materials with high adsorption performance to remove organic pollutants in water.

In order to endow the composites with greater adsorption capacity, in the research, the characteristics of large pore volume and abundant active sites are often achieved by increasing pore size, improving structure, forming good crystal morphology and compounding with other materials. In 2020, Altaf Nazir and others tried to improve the material properties by improving the composite structure. The porous composite with sandwich structure (ZIF-67@CoAl-LDH) prepared by Altaf Nazir had good adsorption capacity for MB (q,m, 57.24 mg g⁻¹), and there was no obvious MB loss after being recycled for four times [206]. Materials with regular crystal forms often show regular performance. Chakraborty synthesized CoAl-LDH/Cu-(tpa) MOF nanocomposites with good crystal forms by in-situ nucleation and growth of Cu-(TPA) MOF on hexagonal LDH nanosheets, and applied them to the adsorption of methyl orange dyes. The reusability test shows that the CoAl-LDH/Cu-(tpa) MOF nanocomposites can be regenerated six times continuously during the adsorption process without significantly reducing the efficiency (Fig. 8j) [207]. Zhi et al. tried to synthesize a new Fe₃O₄/ZnAl-LDH@MIL-53(Al) composite by combining Fe₃O₄ with LDHs@MOFs, which was used to remove azole fungicides in water. [208]. Good crystal morphology, unique core-shell structure, and the synergistic effect between Fe₃O₄ and composites make Fe₃O₄/ZnAl-

### Table 3

<table>
<thead>
<tr>
<th>Material</th>
<th>Pore diameters</th>
<th>Pore volume cm⁻³ g⁻¹</th>
<th>Å</th>
<th>Application</th>
<th>qₑₓₐₓ mg g⁻¹</th>
<th>Removal efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF/LDH/ZIF-8</td>
<td>2.5-8.3 nm</td>
<td>–</td>
<td>156.9</td>
<td>Absorption Cr(VI)</td>
<td>378</td>
<td>99.3% [201]</td>
</tr>
<tr>
<td>NiO-LDH/UiO-66-(Ni)ₓ MOF</td>
<td>–</td>
<td>–</td>
<td>402</td>
<td>Absorption Ti(I)</td>
<td>711.8(T=313K)</td>
<td>98.5% [79]</td>
</tr>
<tr>
<td>Ni₈Co₅LDH/UiO-66-NH₂</td>
<td>2.1</td>
<td>0.91</td>
<td>907</td>
<td>Absorption Ti(I)</td>
<td>601.3</td>
<td>– [202]</td>
</tr>
<tr>
<td>LDH@MgO-76</td>
<td>–</td>
<td>–</td>
<td>79.93</td>
<td>Absorption U(VI)</td>
<td>433.91</td>
<td>70% [56]</td>
</tr>
<tr>
<td>Ni₈Co₅LDH/UiO-66-(Zr)- (COOH)₂</td>
<td>1.9</td>
<td>0.13</td>
<td>41</td>
<td>Absorption Cd(II) and Pb(II)</td>
<td>415.3/301.4</td>
<td>– [209]</td>
</tr>
<tr>
<td>NiO-LDH/UiO-66-(Zr) (COOH)₂</td>
<td>–</td>
<td>0.35</td>
<td>69</td>
<td>Absorption Hg(II) and Ni(II)</td>
<td>509.8/441.0</td>
<td>99%/- [203]</td>
</tr>
<tr>
<td>Ni-MOF(D)/NiO LDH</td>
<td>2.19</td>
<td>–</td>
<td>–</td>
<td>Absorption Br⁻</td>
<td>126.3</td>
<td>– [204]</td>
</tr>
<tr>
<td>ZIF-67/CuBi₂CO₃LDH</td>
<td>–</td>
<td>–</td>
<td>221.55</td>
<td>Absorption I⁻</td>
<td>139.98</td>
<td>– [54]</td>
</tr>
<tr>
<td>MgAl-LDH@Cu(BDC) MOF</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Absorption methyl orange</td>
<td>600</td>
<td>99% [205]</td>
</tr>
<tr>
<td>Ni₈Co₅LDH/LDH/BM2ZIF20</td>
<td>–</td>
<td>0.93</td>
<td>1282</td>
<td>Absorption orange II/Cr(VI)</td>
<td>1173/733</td>
<td>95%/90% [78]</td>
</tr>
<tr>
<td>ZIF-67@CoAl-LDH</td>
<td>–</td>
<td>–</td>
<td>374.3</td>
<td>Absorption methylene blue/methyl orange</td>
<td>57.24/180.5</td>
<td>79%/72.3% [206]</td>
</tr>
<tr>
<td>CoAl-LDH/Cu-(tpa) MOF</td>
<td>69.98</td>
<td>0.836</td>
<td>221.78</td>
<td>Absorption methyl orange</td>
<td>597.32</td>
<td>99.55% (T=328K) [207]</td>
</tr>
<tr>
<td>Fe₃O₄/ZnAl-LDH@MIL-53(Al)</td>
<td>5.2</td>
<td>–</td>
<td>726.1</td>
<td>Absorption triadimefon/epoxiconazole</td>
<td>64.35/71.79 (T=308.5K)</td>
<td>98.2%/98.8% [208]</td>
</tr>
<tr>
<td>Zn-Al LDH@ZIF-8</td>
<td>–</td>
<td>–</td>
<td>1136.87</td>
<td>Absorption CO₂</td>
<td>1.0 mmol g⁻¹</td>
<td>– [209]</td>
</tr>
<tr>
<td>Co-Al LDH@ZIF-76</td>
<td>–</td>
<td>–</td>
<td>22.16(303K)</td>
<td>–</td>
<td>– [210]</td>
<td></td>
</tr>
<tr>
<td>TMU-5@Ni-Ti LDH</td>
<td>16.12Å</td>
<td>0.227</td>
<td>386</td>
<td>Degradation of antibiotics</td>
<td>11.02 mg L⁻¹(45min)</td>
<td>&gt;98% [211]</td>
</tr>
<tr>
<td>Ti-MOF/Ag/NiFeLDH</td>
<td>5.42</td>
<td>0.597</td>
<td>440.2</td>
<td>Degradation of RhB/LVX</td>
<td>–</td>
<td>92%/90% [212]</td>
</tr>
<tr>
<td>NiCoZr LDH@MIL-101(Fc)-NH₂ MOF</td>
<td>2.1-3.1</td>
<td>–</td>
<td>180</td>
<td>Degradation of methylene blue</td>
<td>–</td>
<td>98.2%(10min) [213]</td>
</tr>
</tbody>
</table>
Sustainable Materials and Technologies 37 (2023) e00691

16

LDH@MIL-53(Al) have great application potential in removing azole fungicides in the environment. This section summarizes the research on designing complexes of LDHs and MOFs from the aspects of crystal morphology, structure and pore size, which provides a direction for improving the performance of composite materials in adsorbing organic pollutants in the future.

6.1.4. CO$_2$

The continuous consumption of non-renewable fossil fuels produces "greenhouse gas" CO$_2$, which leads to global warming and climate change. It is urgent to develop effective technologies to remove CO$_2$ on a large scale. Zeolite, activated carbon [221], alkaline ceramics [222], calcium and magnesium oxides [223, 224], etc. have been widely used to adsorb CO$_2$. Composites of LDHs and MOFs are a rational material for CO$_2$ adsorption because of its porous structure and high specific surface area. As early as 2016, Liu synthesized a composite material Zn-Al LDH@ZIF-8 with a specific surface area of 1136.87 m$^2$g$^{-1}$ for CO$_2$ adsorption [209].

In 2018, Yang et al. tried to grow ZIF-67 on the surface of CoAl-LDH in situ to synthesize LDH@ZIF-67 composite nanomaterials, and applied it to the adsorption of carbon dioxide gas (Fig. 8k) [210], the CO$_2$ adsorption capacity of LDH@ZIF-67 can reach 22.16 mg g$^{-1}$ at 30$^\circ$C (Fig. 8l), which is much higher than that of CoAl-LDH. More importantly, the material shows fast adsorption kinetics, and has super high selectivity to CO$_2$ than N$_2$. Meanwhile, Fig. 8m shows the adsorption capacity at 0-100KPa. The application of MOFs@LDHs and LDHs@MOFs material in CO$_2$ adsorption can not only give full play to its excellent characteristics of high adsorption performance, but also effectively alleviate the "greenhouse effect" caused by CO$_2$. The material itself is non-toxic and pollution-free, which accords with the sustainable strategic development concept of green chemistry.

6.2. Degradation

Traditionally, most pollutants are removed from wastewater by adsorption and ultrafiltration. However, low-concentration azo dyes and antibiotics (which can resist microbial and biological oxidation) are difficult to be removed by traditional purification techniques [225].

Reza Abazari et al. designed a composite material: Zn(II) metal-organic skeleton @Ni-Ti layered double hydroxide (Zn-TMU-5@Ni-Ti LDH), which was applied to degrade antibiotics by natural sunlight without oxidizing TMU-5@Ni-Ti LDH [211]. In the study of degrading...
sulfamethoxazole (SMZ) by using composite materials, the removal rate of SMZ by Zn-TMU-5@Ni-Ti LDH composite materials has been significantly improved, and the materials can be reused. The band gap (2.5–2.6 eV) of MOFs [226, 227] and band gap (2.1–2.2 eV) of NiFe LDHs [228] are narrow. Metal decoration and recombinations are two effective ways to improve the charge separation efficiency of MOFs, and the composite material of MOF and LDH will be an ideal photocatalytic material. In 2021, Liu et al. formed a Ti-MOF/NiFe-LDH hybrid on the surface of NH₂-MIL-125 by solvothermal method, and then added plasma silver nanoparticles on this surface to form a new Z-type Ti-MOF/Ag/NiFeLDH photocatalyst (Fig. 8m) [212]. Metal silver nanoparticles promote the transfer of charge, thus improving the photocatalytic performance of Ti-MOF/Ag/NiFe-LDH composites. In addition, the composites also showed good repeatability and stability in the recycling test (after five consecutive test cycles), the removal efficiency of RhB was 92% and that of LVX was 90% (Fig. 8o, 8p). In 2022, Mostafa et al. synthesized a new type of porous hybrid composite ternary NiCuZr layered double hydroxide (LDH)/MIL-101(Fe)-NH₂(MOF) by simple solution casting technology, and then used this composite to degrade methylene blue in water samples by LED [213]. Under the optimum reaction conditions of pH 8, 10 mg NiCuZr@MIL-101(Fe)-NH₂ and 10 min degradation time, the degradation efficiency of methylene blue is higher than 98%.

These sections shows that composites of LDHs and MOFs has obvious degradation effect on dyes in water, and the composite material itself is nontoxic and pollution-free, so it will be an ideal material in the field of photocatalytic degradation.

7. Advanced characterization technology

With the development of science and technology, there are more and more advanced techniques in the characterization of materials. In contrast to the common characterization techniques in the past, where researchers were only able to observe the results at the end of the reaction, advanced in-situ characterization techniques allow for the characterization of all the details of the material changes during the reaction. Many advanced in-situ characterization techniques have been applied in research, including in-situ microscopy (in-situ scanning electron microscopy (SEM), in-situ transmission electron microscopy (TEM)), in-situ X-ray techniques (in-situ X-ray diffraction (XRD), in-situ X-ray photoelectron spectroscopy (XPS), in-situ near-side structure X-ray absorption spectroscopy (XANES), in-situ X-ray tomography imaging), in-situ neutron techniques (in situ neutron diffraction (ND), in-situ neutron depth profiling (NDP)), and in-situ spectroscopy (in-situ Raman spectroscopy, in-situ nuclear magnetic resonance (NMR) and in-situ magnetic resonance imaging (MRI)). In this subsection, we will provide a detailed description of the advanced in-situ characterization techniques that have been used in the study of composites of LDHs and MOFs.

7.1. In situ Drift

In-situ Drift is to obtain the surface reaction information by characterizing the state of in-situ reaction on the catalyst, and then analyze the reaction mechanism. The samples tested by in-situ Drift technology need to be solid powder, which is convenient for direct determination and surface analysis. At the same time, it has the advantages of no need of tabulating and no change of the original shape of samples. Compared with other infrared characterization technologies, in-situ Drift technology will be more tolerant to the requirements of temperature, pressure and atmosphere for in-situ analysis, so in-situ Drift technology has been paid more attention. In the research published by Sun team [229] in 2022, the MIL-100@NiMn-LDH layered structure was constructed in situ for the high selective reduction of CO₂ to CH₄, and the prepared MIL-100@NiMn-LDH showed an excellent CH₄ selectivity of 88.8%(2.84 μmol h⁻¹). In the research process, in-situ diffuse reflectance infrared Fourier transform spectroscopy was used to monitor the intermediate species of CO₂. Many characteristic peaks are shown in Fig. 9a, and the peak at 1558 cm⁻¹ belongs to CO₂*, which means that the active species are converted from absorbed CO₂ molecules; The peak intensity at 636 cm⁻¹ increases with radiation, which is due to the formation of the intermediate COO⁻H⁺. The peaks at 436,1203 and 1101 cm⁻¹ were attributed to CO₂H⁺, CO₂H⁺ and CHO *, respectively. The peaks at 1386 and 1040 cm⁻¹ can be attributed to CH₃⁺ and CH₂O⁺ groups, which are considered as key intermediates in CO₂PR.

7.2. In-situ Raman

In-situ Raman spectroscopy uses the scattering phenomenon that the frequency of incident light changes greatly by material molecules, and excites monochromatic incident light on the electrode surface modulated by electrode potential. By measuring the relationship between the signal intensity and polarization performance of scattered Raman spectrum and the change of electrode potential or current intensity, etc. In 2022, Zhang prepared Ni-MOF/LDH heterostructure and used it to enhance oxygen absorption reaction [77]. Combined with in-situ Drift technology, Zhang determined that metal Ni was the real active center in the process of water oxidation of Ni-MOF/LDH composites. When the potential is set at 0.1-0.4 V, signals are found at 530 and 700cm⁻¹, which are related to the Ni-O tensile mode and iron hydroxide, respectively. When the potential is set at 0.5 V, the Raman spectrum will change significantly, and new peaks will appear at 482 and 561 cm⁻¹, which can be attributed to NiOOH. (Fig. 9b). In similar research, in 2022, Wang introduced monodisperse ruthenium sites that can compete for coordination orientation on conductive MOF/LDH hybrid nanocomposites, which will improve the efficiency of water decomposition in alkaline medium as a whole [124]. In-situ Raman spectroscopy revealed the structural evolution of OER. At 200 mV, a pair of characteristic peaks appear in the range of 450–600 cm⁻¹, and become obvious at 400 mV, which can be attributed to the tensile vibration of MOOH, which proves that it happened in OER in some high-priced metal centers (Fig. 9c). OER occurs in CoNiRu-LDH with high valence active metal, which is more favorable for OH adsorption process and faster electron transfer.

7.3. Summary

Pursuing the characterization of the changes in the reaction process enables us to have a deeper understanding of the occurrence and principle of the reaction. At present, there are only two in-situ characterization techniques used in composites of LDHs and MOFs: in situ DRIFT and in situ Raman. In the future research, more types of in-situ techniques need to be put into the reaction process characterization of materials.

8. Summary and outlook

MOFs and LDHs materials are hot in the direction of energy and environmental protection. The latest research progress of the composites of LDHs and MOFs shows that the synergistic effect between the two materials will make the composite have high porosity, high specific surface area, high conductivity and rich surface active sites. Because of these advantages, composites show many potential applications in energy storage equipment and environmental protection.

In this paper, the important progress of the complex of LDHs and MOFs in energy storage and environmental protection is reviewed. In recent years, researchers are constantly optimizing the properties of the composites from the aspects of structure and surface modification. The properties of unique structure and high active sites strengthen the adsorption and degradation of environmental pollutants, and improve the cycle life, rate performance and energy/power density of electrochemical energy storage devices. It provides useful experience for realizing feasible adsorbents, degradants and energy storage devices (Fig. 10).

Up to now, there have been many researches on composites of LDHs...
Fig. 9. (a) *In situ* DRIFT spectra for MIL-100@NiMn-LDH during CO\(_2\) reduction [229]. Copyright 2022, American Chemical Society. (b) *In situ* Raman spectra of Ni-MOF/LDH at different potentials [77]. Copyright 2021, Elsevier. (c) *In situ* Raman spectroscopic evolution of CoNiRu-NT for OER in 1 m KOH [124]. Copyright 2022, Wiley-VCH.

Fig. 10. Summary diagram of future development direction of MOFs@LDHs and LDHs@MOFs Composites.
and MOFs. Composites with different compositions, morphologies, properties and functions have been successfully synthesized and applied in a wide range of fields. The composites synthesized by developing vacancy, heteroatom doping, heterojunction and other optimization strategies shows better performance than single MOFs or LDHs materials in application. LDHs and MOFs both play their respective roles in composites, which help to overcome the shortcomings of single component and produce strong synergistic effect, thus improving the properties.

Although the application of composites has made some progress, this research field is still developing, there are many challenges, and there is more room for improvement. More efforts are needed to realize the century application of composites materials of LDHs and LDHs. In the future research, this field will face the following challenges and possible research directions:

(i) At present, the composites of LDHs and MOFs are based on one of them, and then the composites of LDHs and MOFs are grown on it. Developing diversified synthetic routes and simplifying the preparation process will be the future research direction.

(ii) In practical research, the composites of LDHs and MOFs are often designed with a variety of structures in which strategies such as heterostructures, cavity and heteroatom doping are designed simultaneously to increase the performance of the material, and future research should focus on designing more kinds of optimization strategies to enhance the performance of composites.

(iii) In heteroatom doping, metallic heteroatoms are designed to be doped into MOFs or LDHs, and more diverse doping of metallic or non-metallic heteroatoms into the composites of LDHs and MOFs are to be developed.

(iv) The research on oxygen vacancy increasing composites properties mentioned in the review proves that vacancy can effectively optimize the properties of composites. Therefore, on the basis of creating oxygen vacancy, exploring other vacancy types is also a future research direction.

(v) Advanced characterization techniques will be very helpful for researchers to know the changes of composites during the reaction process, but only a few literatures have used in-situ characterization techniques. Therefore, in the future research, it is a new research direction to introduce in-situ characterization to explore the reaction process and mechanism of composites.

(vi) Combining the composites of LDHs and MOFs with artificial intelligence computing and simulation techniques for energy and environmental protection is also a new direction for future development.

(vii) The research of applying the composites of LDHs and MOFs to more battery types needs to be designed and developed.

(viii) The composites of LDHs and MOFs has gradually developed in the fields of electric energy storage and environmental protection, but it still takes a certain time to be applied to business. Promoting the practical process of the compound of LDHs and MOFs is one of the directions of future efforts.

Although there are still many challenges in the application of the composites of LDHs and MOFs in practice, there are countless possibilities in this fascinating field. We envisage a bright future of developing the composites of LDHs and MOFs in the sweeping field, which will become an important research field with great potential. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability
No data was used for the research described in the article.

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