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Review

Research Progress and Application of Layered Rare Earth Hydroxides, a Class of Inorganic Layered Compounds with Photoluminescence

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Cite This: *ACS Omega* 2024, 9, 45673−45687

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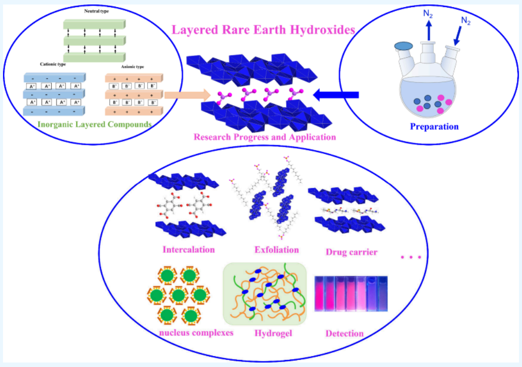


ABSTRACT: Inorganic layered compounds are an important part of organic−inorganic functional nanocomposites and offer plentiful opportunities and possibilities for synthesizing new-style multifunctional materials because they could be intercalated, exfoliated, and swollen. In recent years, as inorganic layered materials with photoluminescence, layered rare earth hydroxides (LRHs) have been extensively studied. Due to their rich functionalization ways, they have been applied or shown potential application value in many fields such as pollution detection, biomedicine, photoelectric energy storage, and so on. On account of the basic physical and chemical properties, the basic structures of LRHs may be regulated through exfoliation and intercalation, which provides more possibilities for synthesizing new multifunctional composite materials and broadening and updating their application fields. In this paper, LRHs are extracted from inorganic layered compounds, and the structure, synthesis, research progress, and application of LRHs are summarized in detail, which lays a great theoretical foundation for further exploration and optimization of the application as a composite functional material in industry, medicine, detection, optoelectronics, and other fields.

1. INTRODUCTION

In recent years, the unique physical and chemical properties of inorganic layered compounds have been featured in many inorganic materials and also attracted more and more favor and attention of researchers. The most representative layered structure and rich interlayer chemical content of inorganic layered compounds enable them to be widely used as adsorption, energy storage, catalysis, and magnetic materials. And, their application fields are in the state of being constantly updated and broadened.[1−7]

Since the first introduction of rare earth elements in 1794 by Gadolin in Finland, they have been closely associated with our lives.[8] Rare earth elements are composed of all lanthanides from lanthanum to lutetium ($[Xe]4f^n5d^m6s^2$ ($m = 0$ or 1, $n = 0{-}14$)), scandium ($[Ar]3d^14s^2$), and yttrium($[Kr]4d^15s^2$), a total of 17 elements,[9] and their unique electron layered structure decides the extraordinary physical and chemical properties. Although scandium and yttrium atoms have smaller atomic numbers and lack the 4f electron shell, the electron configuration $(n-1)d^1ns^2$ is very similar to that of lanthanides, suggesting that their chemical properties may be quite similar. For lanthanides, their signature properties should be their unique optical behavior. The electronic transition inside some lanthanide ions is the root cause of the optical behavior.[10] The typical ions are Sm^{3+}, Eu^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, etc., which often produce strong characteristic emissions due to f−f transitions.

Layered rare earth hydroxides (LRHs) are a relatively unique type of inorganic layered compound with photoluminescence. In 1964, it was realized that rare earth hydroxides might exist in a layered form. But, due to the limited equipment available at the time, no clear structure characterization was obtained. It was not until 2006 that Monge et al. reported LRHs intercalated with organic ions, and since then, LRHs have attracted a lot of attention in the academic sector, as shown in Figure 1.[11] LRHs combine the basic structure−properties of inorganic layered materials with the unique optical properties of rare earth ions. And, the adjustability of the layers and the rich intercalation chemistry lay the foundation for the design and synthesis of multifunctional optical materials. In recent years, many papers about LRHs have been published.[12−17] In this review, the basic properties, preparation methods, research progress, and applications of layered rare earth hydroxides are summarized

Received: July 31, 2024
Revised: October 17, 2024
Accepted: October 21, 2024
Published: November 7, 2024

https://doi.org/10.1021/acsomega.4c07008
ACS Omega 2024, 9, 45673−45687

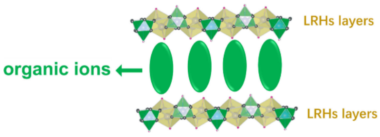


Figure 1. Structure diagram of LRHs intercalated by organic ions. Adapted with permission from ref 11. Copyright 2006 Wiley-VCH.

and analyzed in detail. Compared with previous reviews, this review presents the current research progress of LRHs from a unique perspective. In particular, studies of the host layers and the introduction of interlayer anions and layered rare earth hydroxide composites were analyzed systematically. And, a future possible research direction about photoluminescence can also be prospected, providing a solid theoretical foundation for subsequent research.

2. INORGANIC LAYERED COMPOUNDS

2.1. Definition and Classification of Inorganic Layered Compounds. Generally speaking, inorganic layered compounds[18−21] are a class of inorganic compounds with typical layered structures. Unique structure units are piled up to form the host layer of the compound through the coangulation, coedge, and coplane. Inorganic layered compounds are formed by stacking each layer on top of the other, resulting in a high degree of anisotropy. Terms such as layer thickness and basal spacing are often used to describe the structures of inorganic layered compounds. Layer thickness mainly refers to the thickness of a single layer, and basal spacing represents the distance between the centers of adjacent layers. These concepts provide the basis and convenience for the study of interlayer ion insertion. In terms of interaction, a covalent interaction is the connection between the atoms inside the layer, and there is a weak molecular or ion interaction force between the atoms in the adjacent layer.

Inorganic layered compounds can generally be divided into anionic, cationic, and neutral types according to the electrification of the layers (Figure 2).

2.1.1. Anionic Type. The inorganic layered compounds of anionic type are mainly composed of a positively charged host layer and negatively charged interlayer anions. The existence of interlayer ions is to achieve the charge equilibrium of the whole structure. The typical representative materials are layered bimetallic hydroxide (LDHs),[22−24] layered rare earth hydroxide (LRHs),[25,26] α-type cobalt hydroxide, and nickel hydroxide.[27,28]

2.1.2. Cationic Type. In contrast to anionic compounds, the layers are electronegative, while the interlayer is dominated by positively charged cations. Typical examples include manganese dioxide,[29] transition metal mixed oxides,[30] silicates,[31] and phosphates.[32]

2.1.3. Neutral Type. The layers of neutral inorganic layered compounds are electrically uncharged, so no charged ions need to move between the layers to balance the charges. The layers of compounds are mainly supported by van der Waals forces, and the typical representatives are graphite,[33] vanadium pentoxide,[34] and tin disulfide.[35]

2.2. Basic Properties of Inorganic Layered Compounds. Inorganic layered compounds have unique properties due to the controllability of electrically charged layers and interlayer ions, which are summarized as follows.

2.2.1. Exchangeable Interlayer Ions. There are interlayer ions with corresponding charge and high activity between the positively or the negatively charged layers, which provides a better space for intercalation chemistry. When the concentration of the introduced ions is large enough, the original ions between the layers can be exchanged, and the size of the ions determines the height of the basal spacing, which can be adjusted at any time.

2.2.2. Large Surface Area of the Layers. Layer stacking is characteristic of inorganic layered compounds, and the nanosheets with a large comparative area form after the bulk material is exfoliated. The advantages of nanosheets not only increase the specific surface area of the layered compounds but also lay a solid foundation for the modification and functionalization of the layers.

2.2.3. Stable Host Layers. Regardless of whether the host layer is charged, it is connected by the covalent bond of the structure unit. The atoms in the host layer are mainly linked together by covalent bonds to form a basically rigid two-dimensional layer, while the interactions between the layers are weak, making it easy to modify or functionalize. The stability of the host layer is determined according to different conditions. Under normal states, the layered structure is relatively stable and almost does not change with the change in the chemical environment, regardless of how the interlayer ions change (inset or exchange). For example, many works reported that some organic anions can exchange the interlayer anions in LRHs.[16,36,37] However, some works[38−42] have reported that in the presence of excess anion sources, anions can not only exchange interlayer anions but also exchange coordinated hydroxyl groups and water in the layered structure.

Compared with other inorganic layered compounds, LRHs have all of the above advantages of inorganic layered compounds. Various luminescence properties, excellent characteristics of intercalation and exfoliation, and electrical and magnetic properties are advantages of LRHs, so that more and more scientists are committed to the study of their functionalization. It is worth mentioning that LRHs have both the rich intercalation chemical behavior and the unique controllable luminescence properties of rare earth ions, representing a new class of photofunctional materials. In addition, they can also be calcined to obtain a range of phosphors.[43] However, because of the lanthanide contraction, the degree of hydrolysis of rare earth ions with different radii is

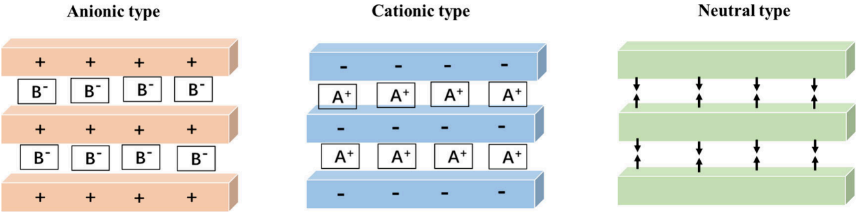


Figure 2. Classification of inorganic layered compounds.

different, causing the different formation range and synthesis conditions of LRHs, and it is difficult to achieve synthesis in the range of a full spectrum rare earth. The stability at higher temperatures is not ideal, the exfoliated nanosheets cannot be stored in formamide for a long time, and so on are the problems the need to be solved for LRHs.

2.3. Research and Application of Inorganic Layered Compounds. The research of inorganic layered compounds mainly focuses on the exfoliated nanolayer, which not only is the core and basic unit of the layered structure but also has the typical properties of specific compounds. At the same time, it has a high specific surface area, providing more opportunities for the functionalization and reorganization of the nanolayer. The layered nanofunctional materials obtained have important application value in the fields of electricity, adsorption, catalytic materials, and so on.[2,3,5]

2.3.1. Electrochemical Field. The layered nanofunctional materials are obtained by exfoliating the inorganic layered compounds and then functionalized and modified, showing good performance in the field of electrochemistry. The typical representatives are graphite oxide, molybdenum disulfide, and layered manganese dioxide. Ji et al. prepared nickel oxide quantum dots/graphene cathode materials by the electrochemical exfoliation method, which greatly increased the energy density.[44] The functional nanomaterials of molybdenum disulfide have excellent electrical properties and have important application value in energy storage devices such as supercapacitors. Ye et al. prepared a pleated graphene/molybdenum disulfide (obtained by hydrothermal exfoliation) complex and combined the conductivity of graphene with molybdenum disulfide nanosheets, which makes it useful as an electrode material for supercapacitors and demonstrate good energy storage properties.[45] The most typical layered manganese dioxide (Birnessite) nanolayer is a good electrochemical material after being functionalized. Brousse et al. successfully synthesized layered manganese dioxide functional composite materials deposited with magnesium ion, which can maintain good specific capacity for cyclic voltammetry testing when used as an electrode material.[46]

2.3.2. Adsorption Material Field. The major advantage of the exfoliated inorganic layered compounds is the high specific surface area, which naturally makes them a new star material in the field of adsorption. In addition to the high specific surface area, the layered manganese oxide is also porous and hydrophilic, showing good adsorption for heavy metals. Linder et al. studied the adsorption of manganese dioxide on arsenic and found the excellent adsorption rate, which was attributed to the complexation between the metal and the layered compounds.[47] Layered bimetallic hydroxides are a wonderful choice of inorganic layered compounds in adsorption materials, which can be used to adsorb heavy metals, toxic gases, and organics in wastewater. Wei et al. studied that layered bimetallic hydroxides with layered morphology have good adsorption properties for Pb^{2+}, and the highest adsorption capacity can reach 421.42 mg/g.[48] In addition to charged layered compounds, neutral layered materials are also a great choice. As a typical example, the functionalized black phosphorus nanosheets show excellent gas adsorption performance[49] and are the preferred materials for the development of various sensors.

2.3.3. Catalytic Materials Field. The catalysis field is also a promising field for inorganic layered compounds. Layered bimetallic hydroxides and molybdenum disulfide are representative catalytic materials. The catalytic activity of layered bimetallic hydroxides is derived from metal ions, hydroxides, and the characteristics of adsorption and intercalation, which are the preferred substrate for various composite materials. He et al. used layered bimetallic nanosheets intercalated by amino acid to coordinate with metal vanadium, and the resulting composite material can be used to catalyze the epoxy reaction in organic chemistry with good catalytic effect.[50] Molybdenum disulfide is a semiconductor material, and the band gap increases in the exfoliated state. Neutral black phosphorus is also an important material in the field of photocatalysis.[51] Xie et al. prepared a black phosphorus quantum dot/graphitic carbon−nitrogen carrier composite material and found that it showed excellent photocatalytic potential in carbon dioxide reduction activation.[52]

3. LAYERED RARE EARTH HYDROXIDES

3.1. Structure and Composition of Layered Rare Earth Hydroxides. The structure and composition of layered rare earth hydroxides are relatively simple and can be understood more intuitively through the general formula. The general formula is $R_2(OH)_{6-m}(A^{x-})_{m/x}\cdot nH_2O$ (R represents rare earth ions with positive trivalent valence; A denotes the interlayer anion; $0.5 \leq m \leq 2.0$), and the LRHs mainly include the types of $m = 1$ and 2.

3.1.1. Layered Rare Earth Hydroxides of Type m = 1. The general formula of LRHs of type $m = 1$ is $Ln_2(OH)_5A\cdot nH_2O$, and it is composed of a positively charged layer and a negatively charged anion.[53] The host layer consists of rare earth ions with positive trivalent valence, hydroxyl groups, and water molecules. And, from a crystallographic perspective, three rare earth ion sites ($Ln1$, $Ln2$, and $Ln3$) and five hydroxyl sites (including three water molecule sites) exist in each crystal cell along with each hydroxyl group bridging neighboring rare earth ions. All phases have two types of lanthanide metal environments containing 8- and 9-fold coordination. One is surrounded by seven hydroxyls and one water molecule (LnO_8), $\{Ln(OH)_7(H_2O)\}$, forming a dodecahedron, while the others are surrounded by eight hydroxyls and one water molecule (LnO_9), $\{Ln(OH)_8(H_2O)\}$, forming a monocapped square antiprism with the capping position occupied by the water molecule.[53] Each LnO_8 polyhedron is linked to two other LnO_8 polyhedra and four LnO_9 polyhedra via the edges. These polyhedron units form a two-dimensional host layer. The anions introduced into the interlayer by ion exchange exist in the form of electrostatic interaction between the layers, which tends to affect the properties of the host LRH layers and also attaches anion-specific properties to the LRHs, making them exhibit rich intercalation chemistry connotations.

3.1.2. Layered Rare Earth Hydroxides of Type m = 2. The $m = 2$ type LRHs were first researched in the 1970s. Compared with $m = 1$ type LRHs, the structure composition of this type is more complex, and the reports about them are rare. $Ln_2(OH)_4SO_4\cdot 2H_2O$, an $m = 2$ type of LRH, has been reported, in which Ln can be Pr, Nd, and a variety of rare earth ions ranging from Sm to Tb.[54]

Their crystal structure analysis shows that the rare earth ions have only one coordination state in the layers, and the coordination number is 9, forming a single polyhedron. The obvious difference with the $m = 1$ type LRHs is that the interlayer anions are also involved in coordination with the layers. A rare earth ion is coordinated with nine oxygen atoms, six of which are provided by hydroxyl groups, two by water, and the last one by the interlayer anion. Coordination is more binding than electrostatic interaction, so it is very difficult for $m = 2$ type LRHs to ion exchange.

William et al. attempted to study the ion exchange of $La(OH)_2(NO_3)\cdot H_2O$ and found that it was ineffective at room temperature.[55] While the interlayer ions could be exchanged at high temperature for 7 days, the exchange process was different from the normal ion exchange through the first dissolution and then precipitation to finally achieve the exchange purpose. Sasaki et al.[54] attempted to perform ion exchange about $RE_2(OH)_4SO_4\cdot 2H_2O$ under hydrothermal conditions but failed. According to the above reports, the $m = 2$ type LRHs do not easily carry out ion exchange because of their complex structure. It is not convenient to regulate their structure and function, so the research hotspots still mainly focus on $m = 1$ type LRHs. And, the content of the following discussion also focuses on $m = 1$ type LRHs.

In addition, some structures have been reported in the literature. For example, Oliver et al. described a cationic erbium-based material $[Er_{12}(OH)_{29}(H_2O)_5][O_3SCH_2CH_2SO_3]_{3.5}\cdot 5H_2O$.[56] As synthesized, the material is water stable and capable of complete organic anion exchange for a variety of α,ω-alkanedicarboxylates. Wu et al. synthesized a series of isomorphic 3D layered rare earth hydroxide frameworks $RE_3(OH)_7(1,5\text{-NDS})$ (RE = Y, Gd, Er, Yb; 1,5-NDS = 1,5-naphthalenedisulfonate) through hydrothermal conditions.[57] The compounds have high thermal stability and can emit strong multicolor photoluminescence, which is a kind of promising multifunctional material. And, Ivanov et al. solved the structure of the first representative of layered rare earth hydroxides intercalated with sulfobenzoate-type anions, namely, layered yttrium hydroxide intercalated with 4-sulfobenzoate with the composition $Y_3(OH)_7(C_7H_4O_5S)\cdot H_2O$.[58] Similarly, Ivanov et al. reported that two methods for preparing ternary layered Gd−Eu−Tb basic sulfobenzoates were implemented: high-temperature anion-exchange reactions and a one-step synthesis. In both cases, the $(Ln)_3(OH)_7(C_7H_4O_5S)\cdot nH_2O$ (Ln = Eu, Gd, Tb) phases were formed.[59]

3.2. Preparation of Layered Rare Earth Hydroxides.

The methods for the preparation of layered rare earth hydroxides are classified into homogeneous precipitation, hydrothermal synthesis, and solvent−thermal synthesis.

3.2.1. Homogeneous Precipitation. The homogeneous precipitation method[60−63] involves the use of specific reagents that cause a controlled change in the degree of supersaturation in the system by generating a precipitate through a slow chemical reaction. The team of Sasaki used this method to obtain LRHs with good morphology and high crystallinity.[64] They reported the synthesis and characteristics of a rare earth-based layered family, $Ln_8(OH)_{20}(NO_3)_4\cdot nH_2O$ with Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Y, synthesized through the homogeneous precipitation of $Ln(NO_3)\cdot xH_2O$ with hexamethylenetetramine. The products were uniform and of high crystallinity. And, the coprecipitation method[65] is an important method for preparing LRHs. It has been reported for the first time that layered rare earth hydroxides can be directly crystallized into nanosheets with a thickness as low as 3 nm through this newly developed "freezing temperature crystallization" technique. The technology can be widely applicable for large-scale production of various LRH nanosheets. And, the LRH nanosheets prepared in this way can be used as a novel precursor to prepare highly transparent ceramics.[66]

3.2.2. Hydrothermal Synthesis. Hydrothermal synthesis[67−77] is a method that utilizes the chemical reaction of substances in aqueous solution to produce a target product under specific temperatures and pressures. Fogg et al.[78] were the first to synthesize a series of LRHs (R = Gd−Lu and Y) by hydrothermal synthesis. However, the method had some limitations and is only suitable for rare earth ions with a relatively small radius. Subsequently, Byeon et al.[79] broke this bottleneck and found that rare earth ions with larger radius, such as Eu^{3+}, could be synthesized into LRHs by adjusting the pH of the solutions in hydrothermal synthesis. From then on, the synthesis of LRHs was essentially unrestricted, which lays the foundation for the design and control of rare earth luminescent materials.

3.2.3. Solvent−Thermal Synthesis. The solvent−thermal method[80−83] for synthesizing LRHs is also a relatively popular method, and the most commonly used solvent is ethanol. The group of Byeon[84] has synthesized $La_2(OH)_5NO_3\cdot 1.5H_2O$ using ethanol as a solvent under heated conditions.

So far, in comparison with the above other methods, homogeneous precipitation is the common method for the synthesis of LRHs owing to its mild conditions, simple operation, and high purity of products. The overall process of the hydrothermal and solvent−thermal method is similar, and it is mainly used to synthesize a series of specific LRHs materials. At present, homogeneous precipitation is a promising synthesis method in industry.

3.3. Research and Application of Layered Rare Earth Hydroxides.

Layered rare earth hydroxides (LRHs), which combine a layered structure and luminescent properties, are the axes of synthesis as well as the design of novel functional optical materials, and they also play a key role in a variety of fields,[39] such as optoelectronics, catalysis, and magnetism. The current research focuses on the controllability and exfoliation of LRH layers, the exchangeability of interlayer anions, and the composability of LRHs with various materials.

3.3.1. Studies of Layered Rare Earth Hydroxide Host Layers. The structure of the host layers of LRHs is the primary factor determining their luminescent properties. And, the current research on the host layers is mainly divided into two directions, namely, controllability of the layer composition and exfoliation of the LRH layers.

3.3.1.1. Controllability of Layer Composition. Rare earth ions exist in the form of coordination in the host layers. Different rare earth ions have different luminescence properties, so it is worth studying them to obtain LRHs with different optical properties by changing the rare earth ion species in layers for acquiring one or more ion-doped host layer. Duan et al. synthesized LRHs with a ternary system (R = Y, Eu, and Tb), and their structures were fully investigated, which also achieved multicolor emission from LRHs.[87] Sasaki et al. obtained ternary layered rare earth hydroxides $(Y_{0.95-x}Gd_xEu_{0.05})_2(OH)_5NO_3\cdot nH_2O$ by flexibly regulating and controlling the layers. Focusing on the effect of Gd^{3+} replacing Y^{3+} on the structure, morphological features, and optical properties of LRHs, it was also found that the successful introduction of Gd^{3+} can selectively sensitize the Eu^{3+} in the C_1 site and enhance the red-light emission of the host layers.[88]

The hydroxyl groups and water molecules on the layers have a quenching effect on the rare earth ions while directly coordinating with them. And, in order to overcome this, the layers can be calcined to obtain rare earth oxide phosphors, which greatly increase their photoluminescence intensity. The

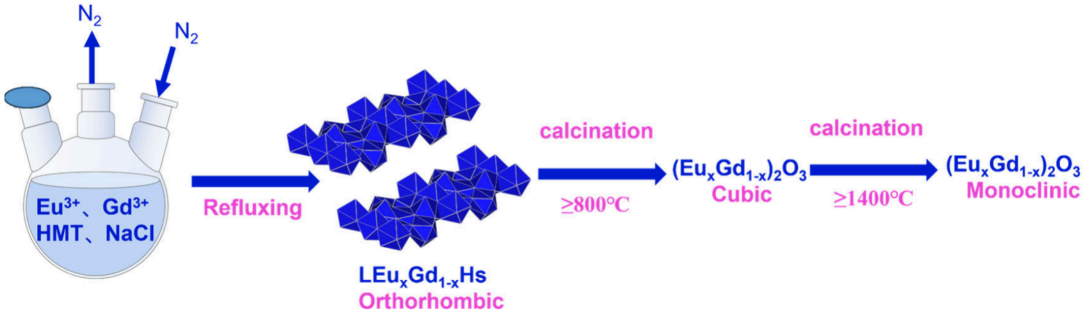


Figure 3. Preparation process of $(Eu_xGd_{1-x})_2O_3$ (hexamethylenetetramine is short for HMT). Adapted with permission from ref 85. Copyright 2010 American Chemical Society.

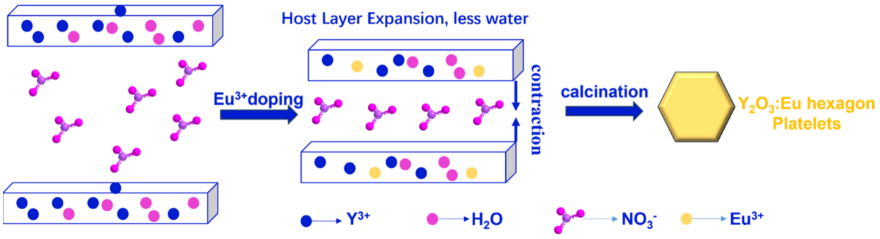


Figure 4. Preparation process of $(Y_{1-x}Eu_x)_2O_3$. Adapted with permission ref 86. Copyright 2010 American Chemical Society.

Sasaki group calcined LRHs codoped with Eu and Gd to obtain $(Eu_xGd_{1-x})_2O_3$ (Figure 3) with a photoluminescence intensity that is not inferior to that of the commercial phosphors.[85] Bando et al. calcined LRHs codoped with Eu and Y above 400 °C to obtain $(Y_{1-x}Eu_x)_2O_3$ with a cubic structure and strong red-light emission while maintaining its original morphology (Figure 4).[86] Ternary layered gadolinium−europium−terbium basic chlorides were synthesized using a facile hydrothermal−microwave technique by Ivanov et al. And, the intercalation of the 4-sulfobenzoate anion into the interlayer space of LRHs led to the sensitization of Tb^{3+} and Eu^{3+} luminescence.[59] Williams et al. reported layered rare earth hydroxides as multimodal medical imaging probes. They incorporated Gd and Tb into LRHs in varying molar ratios (1:3, 1:1, and 3:1) and assessed the combined magnetic relaxivity and phosphorescence properties of the resultant LRH materials, which exhibited a strong phosphorescence signal, therefore holding great promise as potential multimodal medical imaging probes.[89]

3.3.1.2. Exfoliation of LRH Layers. The layered structure of LRHs is supposed to be the most unique compared with ordinary rare earth materials, and the exfoliation of the layered structure into single-layer or few-layer nanosheets not only achieves the dimensional change but also greatly increases its specific surface area, which opens a new pathway again for the synthesis and design of new optical functional materials. Sasaki et al. achieved the exfoliation of LRH nanosheets in formamide for the first time and pointed out that only the DS^- ($C_{12}H_{25}OSO_3^-$) intercalated LRHs could be exfoliated into 2D nanosheets.[90] Since then, the academic community has been enthusiastic about the research on LRH 2D nanosheets. However, The LRH nanosheet crystallites are gradually dissolved due to the slow hydrolysis of formamide to formic acid, which is not favorable for long-period storage,[12,91−93] which is also worth studying to maintain the long-term stability of nanosheets. The long-term (longer than 30 days) stability of dispersions in formamide of layered (Y, Gd, and Eu) hydroxides intercalated with dodecyl sulfate anion has been studied for the first time by the Baranchikov team. It has been shown that layered yttrium, gadolinium, and europium hydroxides intercalated with dodecyl sulfate anion react with formamide to form $[Ln(HCOO)_3\cdot 2(HCONH_2)]$ (Ln = Y, Gd, or Eu). Obtained data indicate that the colloidal solutions of quasi-2D crystals of LRHs in formamide remain stable for several days.[91] Another frequently used method for exfoliation of LRHs is the exfoliation in toluene.[94] This is the case for LRHs intercalated with oleate anions, and the process is conducted under sonication. The interaction with toluene causes the solvation of the hydrophobic fragments of the intercalated anions, weakening the van der Waals interactions between them. Strong stirring and ultrasonic treatment of the suspension thus prepared are conducive to the formation of colloidal solutions containing exfoliated particles. The colloidal solutions remain stable for a month or more.[16]

After the layers were exfoliated, studies on the reassembly and self-assembly of the LRHs nanosheets emerged. Byeon et al. exfoliated two different LRHs nanosheets and then self-assembled them with $Mo_7O_{24}^{6-}$, obtaining rose-petal-shaped structures. And, it was also found that $Mo_7O_{24}^{6-}$ could replace hydroxyls on the layers, reducing the quenching phenomenon brought about by hydroxyls and obtaining stronger photoluminescence emission.[95]

The rearrangement process of LGdH nanosheets and DS^- was also surveyed, and it was proved that the coordination of DS^- with the layer was different at different pH values, which resulted in different structures as well as optical properties of the layers obtained by rearrangement (Figure 5).[96] Yang et al. investigated the rearrangement process of LTbH nanosheets and DS^- (Figure 6), and the hydroxyl groups of the layers were found to be replaced by DS^- ions in large quantities, yielding a new type of layered rare earth hydroxide. Thus, the optical properties were also changed due to the new structure with the photoluminescence intensity greatly enhanced.[97]

In addition to the most basic structure and optical properties of LRH nanosheets that are highly favored by researchers, they are also promising magnetic materials. The unique nuclear magnetic resonance (NMR) relaxation properties of LGdH nanosheets have been reported to have the potential to be used

https://doi.org/10.1021/acsomega.4c07008
ACS Omega 2024, 9, 45673−45687

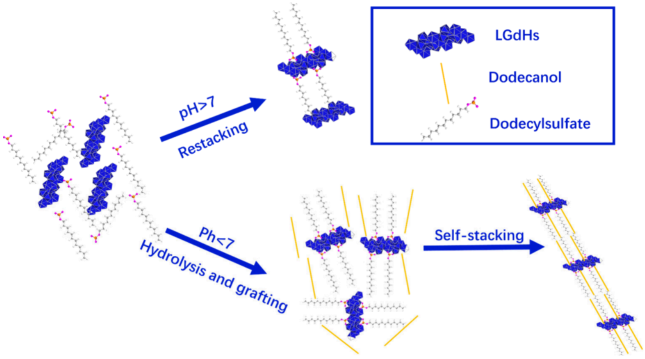


Figure 5. Self-assembly diagram of LGdHs. Adapted with permission from ref 96. Copyright 2011 Royal Society of Chemistry.

as a positive contrast agent.[98] Byeon et al. found that LGdH nanosheet dispersions can promote the magnetic relaxation properties of water protons, which can be used for the synthesis of novel contrast agents with great potential for application in the medical field.[99]

And, Zhu et al. reported that the layered gadolinium hydroxide nanoplates doped with Ce and Tb (LGdH:Ce, Tb NPs) are excellent contrast agents (CAs) and exhibited multifunctionality suitable for computed tomography and fluorescence bioimaging. Their performance as a contrast agent in ultrahigh-field MRI (magnetic resonance imaging) of subcutaneous liver tumor-bearing nude mice was investigated, demonstrating its ability to be used as a negative target contrast agent to distinguish hepatic carcinoma from healthy tissues.[100] Ma et al. reported that unilaminar LGdH and Ti_3C_2 nanosheets were face-to-face restacked into an LGdH/Ti_3C_2 (GTC) hybrid, which exhibited enhanced near-infrared (NIR) light absorption and MRI performance, broadening the application of both MXenes and LRH nanosheets toward biotherapy and providing a general strategy to design photothermal therapy and MRI contrast agent materials based on 2D nanomaterials.[101]

Huang et al. developed a superior layered rare earth hydroxide adsorbent, ultrathin $Y_2(OH)_{4.86}Cl_{1.44}\cdot1.07H_2O$ nanosheets, to achieve the effective removal of perfluorooctanoic acid (PFOA). The nanosheets were prepared by a rapid thermal exfoliation process, which exhibited a rapid removal of PFOA with an ultrahigh adsorption capacity (957.1 mg/g).[102]

3.3.2. Anion Intercalation of Layered Rare Earth Hydroxides.

The positively charged layers of LRHs predetermine the electrification of the interlayer anions, and the tunability and variability of the interlayer anions endow them with rich intercalation chemistry connotations. The change of the anions can affect the structure and optical properties of LRHs. There are two main intercalation types, namely, organic anion intercalation and inorganic anion intercalation.

3.3.2.1. Organic Anion Intercalation.

In LRH layers, hydroxyl groups and water in coordination with rare earth ions would also have a quenching effect on their photoluminescence performance, resulting in the photoluminescence intensity of LRHs being not ideal. Therefore, it is one of the commonly used effective means through the antenna effect to make the sensitizer into the interlayer for transferring energy to the rare earth ions in order to enhance the photoluminescence intensity.

Organic ions often act as sensitizers, and there are two conditions that need to be met for becoming interlayer organic sensitizers of LRHs. The first condition is that the organic ions need to be negatively charged, understood from the perspective of functional groups, generally with $-COO^-$, $-SO_3^-$, etc., to ensure that they can be inserted into the interlayer for maintaining the charge balance. Another condition is energy level matching. The difference between the triplet state energy level of organic sensitizers and the rare earth ion emission state energy level should be within a certain range to ensure that the energy can be transferred smoothly. At present, the studied organic anions mainly include dodecyl sulfate, benzoic acid, coumarin, amino acids, 1-naphthoic acid, 2-picolinic acid, pyrrole-2-carboxylic acid, 2-furoic acid, ibuprofen, naproxen, diclofenac, cephalexin, aspirin, 8-hydroxypyrene-1,3,6-trisulfonic acid, bipyridine dicarboxylic acid, and so on.[12,36,103−111]

The concept of interlayer sensitization about LRHs originated from the study of layered bimetallic hydroxides (LDHs) doped with rare earth ions. Xu et al. sensitized the Tb^{3+} ions in the layers of LDHs by intercalating 4-biphenylacetic acid anions and could achieve the emission of light from blue to green, not only enhancing the photoluminescence intensity of the Tb^{3+} but also improving its quantum yield.[112] Such an inorganic−organic hybrid system provides new opportunities to utilize and develop multifunctional luminescent materials (Figure 7). Subsequently, Lei et al. reported the insertion of four sensitizing ions (naphthalene-1,5-disulfonate (15-NDS), naphthalene-2,6-dicarboxylate (26-NDC), benzoic acid (BA), and terephthalic acid (TA)) into Eu^{3+}-doped LDHs.[37] They found that carboxylate ions had stronger sensitizing effects than sulfonate ions, and the sensitizing effect was ranked in descending order of sensitizing effect (TA > 26-NDC > BA > 15-NDS).

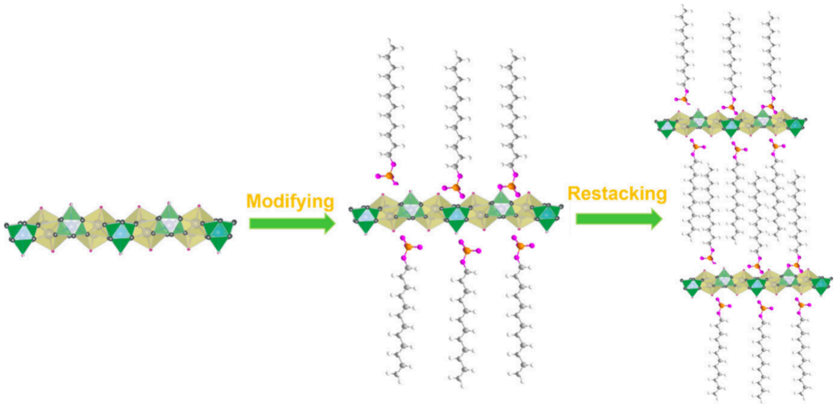


Figure 6. Schematic diagram of surface modification and rearrangement of LRHs. Adapted with permission from ref 97. Copyright 2017 Wiley-VCH.

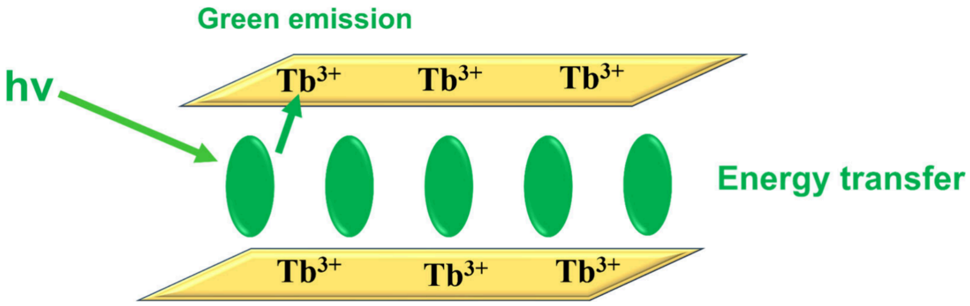
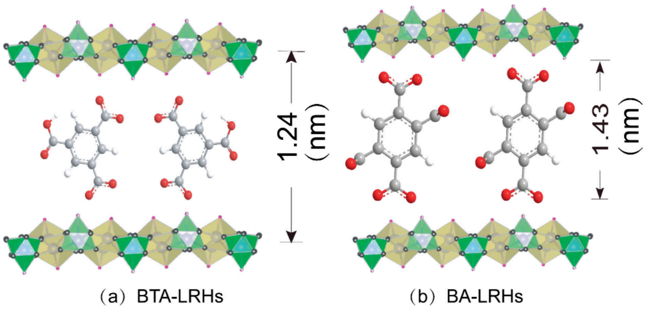


Figure 7. Sensitization of Tb^{3+} ions in the layer of layered bimetallic hydroxides (LDHs) by the interlayer 4-biphenylacetate anions. Adapted with permission from ref 112. Copyright 2009 American Chemical Society.

With the in-depth study of LDH layers doped with rare earth ions sensitized by organic ions, researchers have gradually focused on sensitizing and embellishing the LRH layers. Yang et al. inserted tribenzoate and tetrabenzoate as sensitizers into the LRH layers (Figure 8) and found that the energy transfer to the rare earth ions of the layers was more significant for the red-light emission.[104] Ma et al. used the same concept to introduce benzoate derivatives into LTbHs and achieved high-strength green-light emission (Figure 9).[113]



(a) BTA-LRHs (b) BA-LRHs

Figure 8. Schematic diagram of 1,3,5-benzenetricarboxylic acid (BTA) and 1,2,4,5 benzenetetracarboxylic acid (BA) intercalated into LRHs as sensitizers. Adapted with permission from ref 104. Copyright 2014 Elsevier.

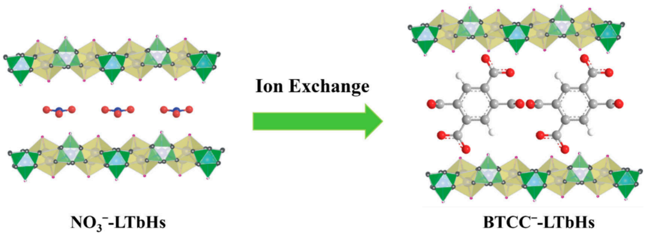


Figure 9. Schematic diagram of 1,2,4,5-benzenetetracarboxylic acid anions ($BTCC^-$) intercalated into layered terbium hydroxides (LTbHs) as sensitizers. Adapted with permission from ref 113. Copyright 2017 Elsevier.

In recent years, Yang et al. reported that eight kinds of (hetero)aromatic anions terminated with $-COO^-$ were intercalated into the interlayer of layered europium hydroxides (LEuHs) as sensitizers for enhancing Eu^{3+} PL via ion exchange with NO_3^-. Different anions showed different orientations in the interlayer, which can result in different energy transfer effects (Figure 10).[36]

In addition to benzoate derivatives, coumarins are also a class of commonly used sensitizers. Ma et al. employed coumarin-3-carboxylic acid as a sensitizer to allow the photoluminescence intensity of LEuHs nanosheets to be significantly improved (Figure 11), which also opened up a new avenue for the selection of the sensitizer type for the interlayer.[106] Although most of the research efforts have focused on the enhancement of luminescence by organic ions as sensitizers, a few studies have also reported the mechanism and process of organic ions as quenching agents.

Ma et al. introduced amino acids into the layers of LRHs and found that the amino groups could have a quenching effect on rare earth ions Eu^{3+}. And, the method is expected to be used for the detection of amino acids in biological as well as food systems (Figure 12).[105]

Fogg et al. explored the application value of layered gadolinium hydroxide (LGdHs) for drug delivery and magnetic resonance imaging by inserting three drugs (ibuprofen, naproxen, and diclofenac) into the LGdHs, departing from the limitations of the adjustment of the optical properties.[107] Yang et al. explored the drug-loaded and bactericidal behaviors of Eu^{3+}-doped layered gadolinium hydroxides (LGdHs:Eu) as optical carriers through the intercalation and release of cephalexin (CE). The PL intensity of CE^-−LGdHs:Eu obviously decreased because of the quenching effect of CE^- in the intercalation state. CE^-−LGdHs:Eu showed excellent bactericidal properties in both in vivo and in vitro experiments and also displayed the potential application value of layered rare earth hydroxides in the medical field (Figure 13).[108] Gu et al. demonstrated the first example of the intercalation of naproxen (NPX) into layered europium hydroxide (LEuH) and investigated the structure, chemical composition, morphology, luminescence properties, cytotoxic effects, and controlled-release behaviors. The cytotoxic effect of LEuH could be observed, which reveals that the LEuH has low cytotoxic effects on most cells.[114] Later, they investigated the cytotoxic effects and controlled-release behaviors of the layered terbium hydroxide (LTbH) intercalated with aspirin (ASA).[109] Shi et al. synthesized a novel Tb^{3+}-activated layered lutetium hydroxide. Organic anions (ibuprofen) were intercalated in LLuH:Tb, which effectively promoted the characteristic emission of Tb^{3+}.[115] 3-Amino-benzenesulfonic acid (AS) was intercalated into layered terbium hydroxide by Gu et al., which was successfully applied for dipicolinic acid detection.[116] Both *trans*- and *cis*-cinnamate anions were intercalated in layered yttrium hydroxide (LYH) by Ivanov et al., and the interlayer distance of *trans*-cinnamate-intercalated layered yttrium hydroxide suspended in isopropanol changed from 21.9 to 20.6 Å.[117]

Gui et al. successfully inserted anionic fluorescent dye molecules (8-hydroxypyrene-1,3,6-trisulfonic acid, HPTS) into the interlayers of the LYH structure through a straightforward

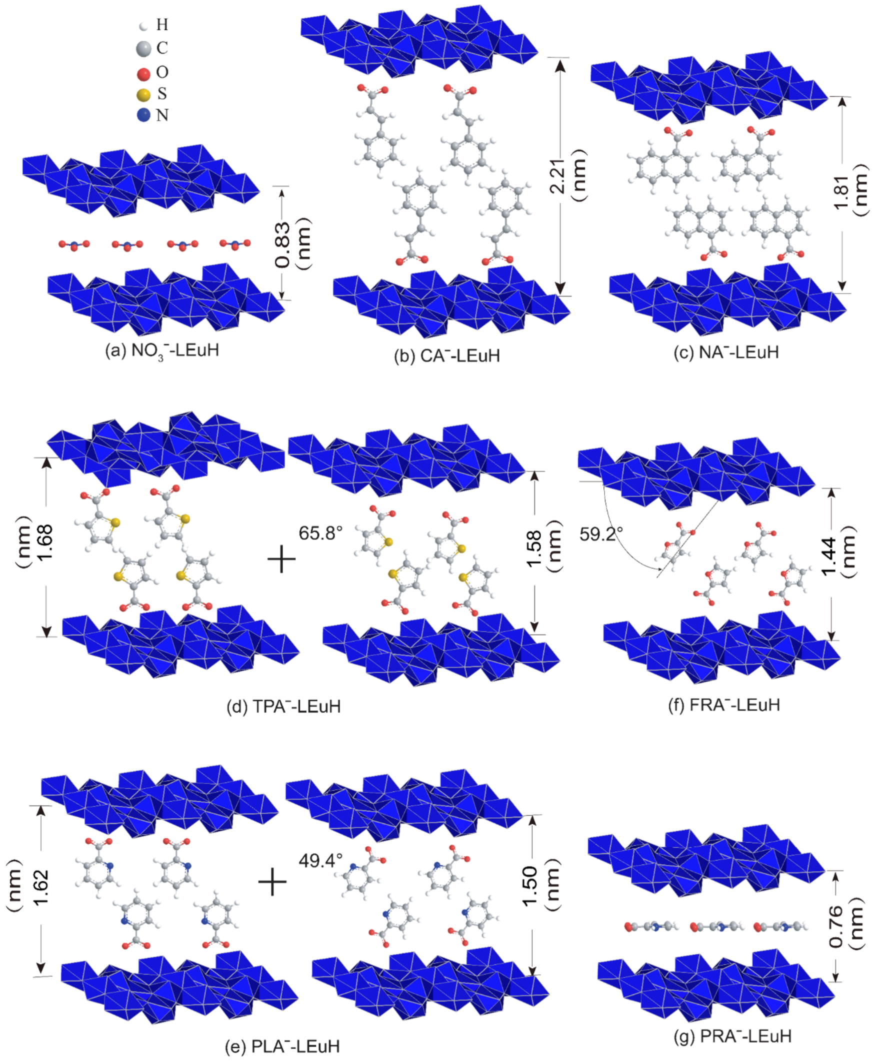


Figure 10. Schematic diagram of the different sensitizer (cinnamic acid anions (CA$^-$), 1-naphthoic acid anions (NA$^-$), 2-picolinic acid anions (PLA$^-$), pyrrole-2-carboxylic acid anions (PRA$^-$), 2-furoic acid anions (FRA$^-$), and 2- thiophenecarboxylic acid anions (TPA$^-$)) orientations between the LEuH layers with respective basal spacing (in nanometers). Adapted with permission from ref 36. Copyright 2019 American Chemical Society.

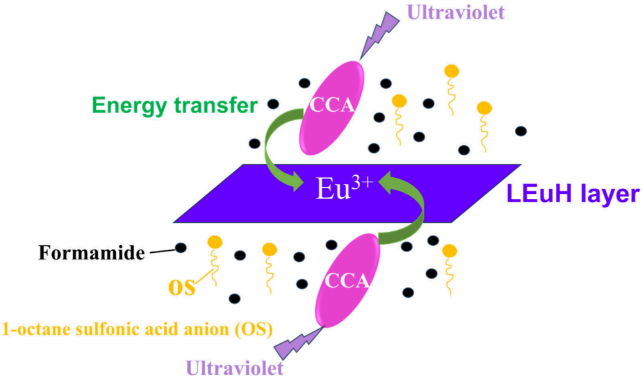


Figure 11. Schematic diagram of coumarin-3-carboxylic acid anions (CCA) as the sensitizer to enhance the PL intensity of LEuHs. Adapted with permission from ref 106. Copyright 2017 Royal Society of Chemistry.

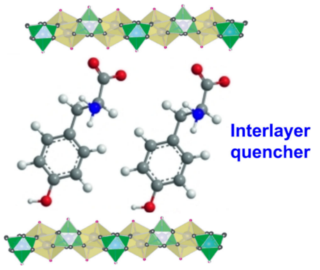


Figure 12. Schematic diagram of amino acids intercalated into the interlayers of LRHs as the quenchers. Adapted with permission from ref 105. Copyright 2012 Wiley-VCH.

one-step ion-exchange method, which enables convenient, rapid, and accurate detection of nitroaromatic organic toxins and harmful substances.[110] Zhang et al. introduced 2,2′-bipyridine-4,4′-dicarboxylic acid and 2,2′-bipyridine-5,5′-dicarboxylic acid into LGdHs, successfully obtaining a nanohybrid phosphorescent photosensitizer, which provides a novel platform for designing a high-performance hydrotalcite-intercalated nanohybrid phosphorescent photosensitizer through coordination induction to regulate the layer microenvironment.[111]

3.3.2.2. Inorganic Anion Intercalation. Compared with organic anions, inorganic anions are smaller in size. The smaller steric hindrance is more favorable for interlayer anion insertion. Most anions such as F$^-$, Cl$^-$, I$^-$, OH$^-$, ClO^{3-}, S^{2-}, CO$_3^{2-}$,

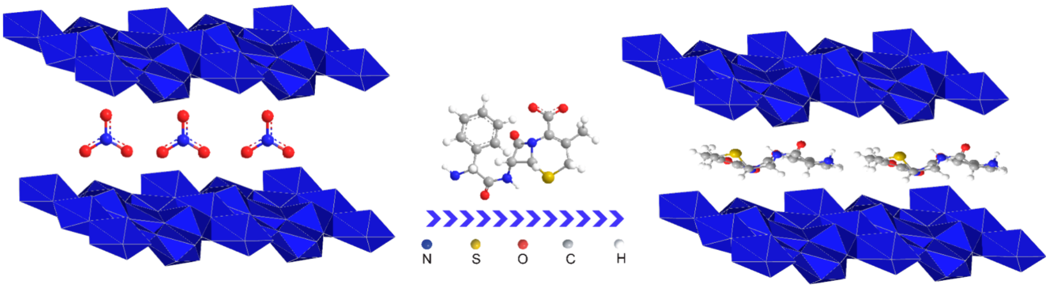


Figure 13. Schematic diagram for the structures of NO_3^-−LGdHs:Eu (Eu^{3+}-doped layered gadolinium hydroxides intercalated by NO_3^-) and CE$^-$−LGdHs:Eu (Eu^{3+}-doped layered gadolinium hydroxides intercalated by cephalexin anions). Adapted with permission from ref 108. Copyright 2021 Elsevier.

SO_4^{2-}, etc., have been introduced into LRHs.[118] However, few of them have an obvious enhancement or quenching effect on the layers.

Byeon et al. reported the discovery that WO_4^{2-} can selectively sensitize Tb^{3+}-doped LRHs, showing strong green-light emission.[119] This discovery opened up a brand-new pathway for sensitizing LRHs by inorganic anions and also provided a new optical method to achieve trace detection of WO_4^{2-} ions.

Later, Byeon et al. again reported that vanadate can produce an antenna effect on Eu^{3+}-doped LGdHs. More notably, spacer molecules with long alkyl chains greatly facilitate the entry of vanadates into the interlayer surface of LGdH:Eu, enhancing the luminescence of Eu^{3+}. Vanadate can exist in different forms at different pHs in aqueous solution through oligomerization as well as protonation reactions. And, it is of vital importance to detect vanadate in a wide pH range, and this antenna effect of light trapping provides a new idea for solving the problem of detecting vanadate.[120]

Yang et al. discovered that a mild and effective way working over a wide pH range (from 2 to 12) to detect selectively trace amounts of molybdate ions of aqueous solutions in a short time was realized by the antenna effect between the molybdate ions and LEuHs. When the quantity of molybdenum adsorbed was within a certain range, the PL increase had an exponential function relation with the adsorption quantity, providing a new idea to detect molybdate ions in industry.[121] Byeon et al. reported that Tb^{3+}-doped LYHs can adsorb CrO_4^{2-}, and the quenching effect of Cr(VI) causes the photoluminescence intensity of LYH:xTb to be greatly weakened, which can be used for the detection of heavy metal pollution at low concentrations.[122]

Yu et al. reported that through taking advantage of the valency changing ability of Ce^{3+} to alternately introduce permanganate and vitamin C, Ce^{3+}-doped LYHs can be used as a new type of "on/off" optical sensor by the artful use of photoluminescence quenching and repair, laying a foundation for the realization of multifield applications of LRHs.[123]

In addition to investigating the antenna effect of inorganic ions on the layers, some reports have introduced only specific inorganic anions for detailed structure investigations. Xiao et al. systematically investigated the adsorption of LRHs for selenite and selenate ions and found that the maximal adsorption for selenite was significantly higher than that for selenate. Selenate ions formed outer-sphere complexes in the interlayer space, and the selenite ions is directly bound to the Y^{3+} center of the positively charged layer by strong bidentate binuclear inner ring complexation. The different positions of the two lead to different adsorption amounts.[124]

Detailed studies of the adsorption kinetics, isotherms, selectivity, and desorption of selenite and selenate at pH = 7 and 8.5 were also carried out, expanding the application of LRHs in the field of adsorption of heavy metals in wastewater treatment resources.

The dodecaborate was intercalated into LRHs through a microwave-assisted hydrothermal method for the first time, which was reported by Ivanov et al. The structure and composition of this compound were determined by a series of characterization means.[125] And, it was found that dodecaborate was indeed inserted into the interlayer, which broke the usual inherent knowledge of researchers and realized the introduction of the boride into LRHs. However, the effect on the optical properties of the LRHs must be further investigated in detail.

In addition to the above discussion, a simple and effective ion-exchange method was proposed by Gui et al. for the introduction of stable and ultrahigh proton conductivity in layered rare earth hydroxides.[126] They studied the ion-exchange process involving $H_2PO_4^-$ in the LRHs. Test analyses revealed that the exchange of $H_2PO_4^-$ not only does not disrupt the layered structure of LRHs but also creates more active proton sites and channels necessary for proton transport, thereby creating a high-performance proton conductor (LRH−$H_2PO_4^-$).

3.3.3. Research and Applications of Layered Rare Earth Hydroxide Composites. The exfoliation of LRH layers creates new opportunities for the preparation of multifunctional composites. The electropositivity of the layer itself and the polyhydroxyl structure are the basis and premise of its composite with various materials.

There are many kinds of LRH composite materials, which can be divided into three types: compounded with polymers, compounded with inorganic nucleus, and compounded with metal complexes.

3.3.3.1. LRHs/Polymer Complexes. LRHs can be composited with various polymer materials to prepare optical materials with specific functions by using electrostatic interaction, hydrogen bonding, and other acting forces, which improves the stability of the LRHs themselves and also adds optical properties to the composites.

Li et al. reported a tunable layered rare earth hydroxide/polyacrylamide hydrogel ($LTb_{1-x}Eu_xH$/PAM) by an in situ polymerization process for the first time. The composite hydrogels have multicolor photoluminescence tunable properties (from green to blue violet), a long luminescence lifetime, and high quantum efficiency, while the photoluminescence intensity can be tuned by the composition of the LRHs or their concentration.[127]

Subsequently, Li et al. reported another LRHs/polyacrylamide hydrogel with highly color-tunable photoluminescence

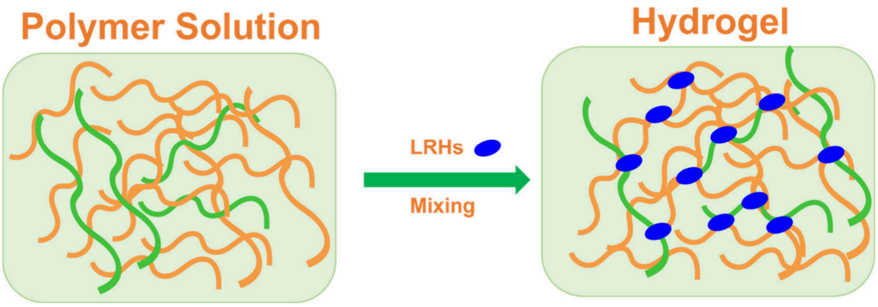


Figure 14. Structure diagram of layered rare-earth hydroxide (LRH) composite hydrogels. Adapted with permission from ref 130. Copyright 2020 American Chemical Society.

and energy transfer effect. The hydrogels contained rare earth ions Gd^{3+}, Eu^{3+}, and Tb^{3+}, and a linked energy transfer pathway was found: LGdHs → sensitizer → Tb^{3+} → Eu^{3+},[128] which brought the LRH hydrogel into the view of researchers once again. Zhang et al. synthesized a composite hydrogel consisting of LEuHs/poly(vinyl alcohol) through in situ polymerization and found that the hydrogels exhibited a unique photoluminescence quenching response to different ammonia environments. And, the whole process could be identified by the naked eye. The quenching was due to the water molecules as well as ammonia vapor, and the photoluminescence self-healing behavior grew as the vapor was volatilized, which opens up a new pathway for the optical multifunctionality of LRH hydrogels.[129]

Recently, Feng et al. prepared sodium alginate/sodium polyacrylate/LRH composite hydrogel materials using LRHs as a linker and a fluorescent light source (Figure 14).[130] The prepared LRH-based composite hydrogels showed a good 3D printing performance at room temperature. And, when exposed to different humidity conditions, the hydrogels exhibited electromechanical properties related to humidity. It was also discovered that the introduction of LRH nanosheets could achieve multiple functions of the hydrogels. When lanthanide ions Eu^{3+} and Tb^{3+} were introduced into the LRHs, the hydrogels could exhibit highly tunable multicolor photoluminescence properties by adjusting the composition of the LRHs. Meanwhile, a transparent skin-like motion sensor was fabricated on the basis of the printed hydrogel for monitoring human motion. This study opens the way for the application of multifunctional hydrogels in the field of sensing.

Yang et al. focused on novel nanosheets of layered rare earth hydroxides/poly(vinyl alcohol) hydrogel (NSs−LEu$_x$Tb$_{1-x}$Hs/PVA hydrogel (x = 0−1)) prepared via an environmentally friendly method. And, novel organic−inorganic nanocomposites with a uniform dispersion of NSs that were noninterfering and had multicolor PL behavior were obtained. This work enables the preparation of luminescent polymer hydrogels with multicolor PL, which is expected to be practical in industrial fields (Figure 15).[131]

In addition to gels, Byeon et al. formed luminescent thin-film materials by combining LRHs with polyethylene glycol. And, the high mechanical strength as well as optical tunability expanded their applications in several fields.[132] Tang et al.[133] used solvent casting to prepare novel transparent and color-tunable nanocomposite thin-film devices based on the combination of LRHs with poly(methyl methacrylate) (PMMA). As a sensitizer, polymer materials improve the optical properties of hybrid phosphors, thereby more than doubling the photoluminescence quantum yield of the film compared with hybrid phosphors.[134] The results open a new way for the preparation of LRH-based tunable color-emitting nanocomposite films, which have a promising application in various optical devices.

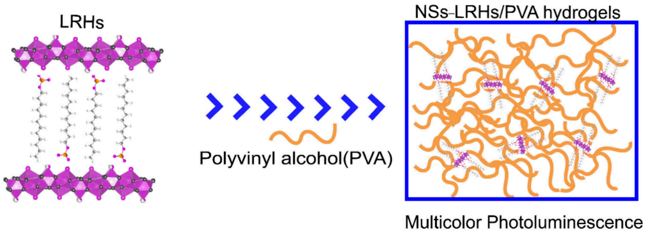


Figure 15. Preparation process of nanosheets of layered rare-earth hydroxides/poly(vinyl alcohol) hydrogel (NSs-LRHs/PVA hydrogel). Adapted with permission from ref 131. Copyright 2021 Elsevier.

3.3.3.2. LRHs/Inorganic Nucleus Complexes. LRH nanosheets can be encapsulated on the outside of an inorganic nucleus to assemble specific core−shell structural materials with novel optical functions. Positively charged LRH nanosheets can be composited with modified negatively charged inorganic core materials by electrostatic interaction. Nano-SiO$_2$ is a more ideal composite object among many inorganic core materials due to its excellent performance and suitable size.

The Byeon groups composited negatively charged SiO$_2$ spheres modified by phosphate with Eu^{3+}-doped LGdH nanosheets and calcined the nanosheets to obtain core−shell structures with red-light emission.[98]

Subsequently, Yang et al. coated LEuH nanosheets on modified SiO$_2$ spheres and then aligned them to form two-dimensional colloidal crystals with intense red-light emission (Figure 16).[135] The core−shell structures of LRHs have not been studied and reported so much yet, but their unique structure and optical properties will be of great research value in the future.

3.3.3.3. LRHs/Metal Complex Composites. The combination of LRHs with metal complexes to form relatively new composites has been mainly applied to optical temperature sensors, etc. Zhu et al. dispersed Y/Eu binary layered rare earth hydroxides in formamide, exfoliated them into ultrathin nanosheets, and grafted Tb(III) complexes onto the exfoliated nanosheets to obtain composite layered nanomaterials. Applied to temperature sensors, which were tuned from 77 to 360 K and exhibited photoluminescence emission ranging from green to pink, as well as high sensitivity and temperature dependence, it has the potential to open up new fields of material functionality.[136]

Similarly, Zhu et al. inserted another type of complex of Tb(III) into Y/Eu binary LRHs, and the composite LRHs could emit light dependent on temperature adjustment, showing photoluminescence emission from green to pink by adjusting

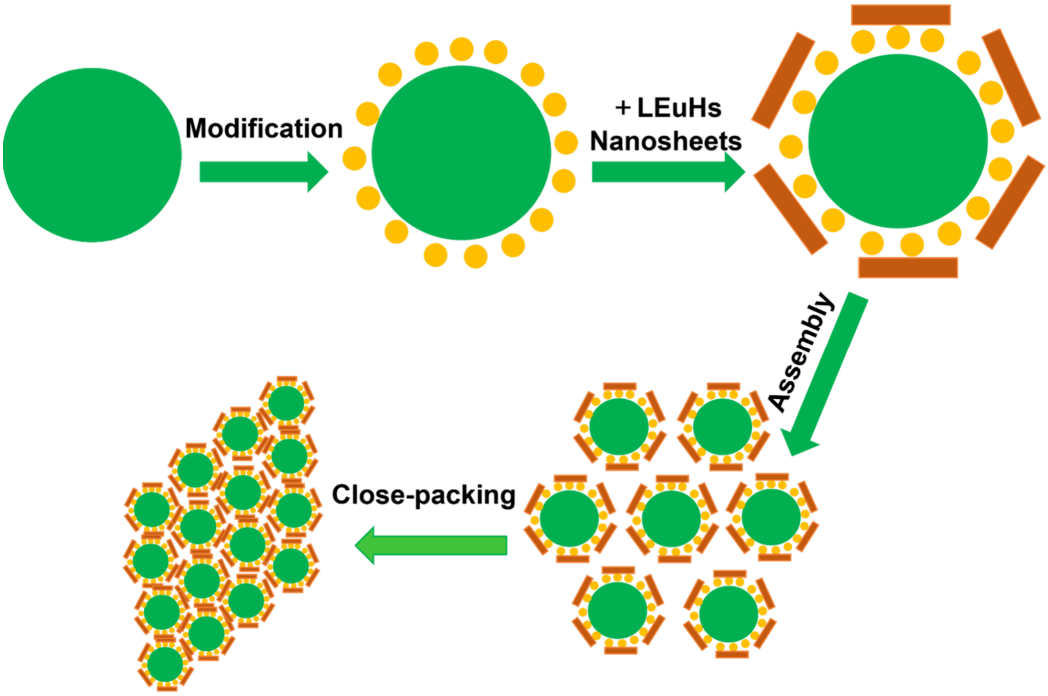


Figure 16. Schematic diagram for the formation of two-dimensional colloidal crystals (LEuHs nanosheets are layered europium hydroxides nanosheets). Adapted with permission from ref 135. Copyright 2019 Royal Society of Chemistry.

the temperature change (from 77 to 450 K). This can be applied to novel optical temperature sensors for 1D and 2D thermal imaging, which can reversibly undergo repeated thermal cycling.[137]

The research on LRHs has involved plentiful fields, focusing on the change of interlayer ions and the composite materials of LRHs, which makes it possible to synthesize new functional luminescent materials. At present, the energy transfer mechanism of sensitizers in different materials to LRHs can be further explored. And, due to LRHs' excellent interlayer capacity, it also needs further research for applications in the field of drug loading and sterilization.

4. CONCLUSIONS

In summary, the basic structure, properties, preparation methods, and current research directions of layered rare earth hydroxides are summarized and analyzed in detail. LRHs are an outstanding choice for preparing a variety of functional organic and inorganic complex materials with different characteristics due to their unique layered structure and optical properties, and they are currently mainly used in detection, adsorption, medical treatment, magnetism, and other fields. However, the research on layered rare earth hydroxides has not stopped, and many directions still need to be further explored. For example, the quantitative relationship between the structure orientation of interlayer guest ions and the photoluminescence intensity of the layers is not clear yet. At present, it has emerged as an optical probe in the field of water resources detection; whether the probe effect can be applied to agricultural and food detection through the antenna effect is also an urgent need to be explored. The research on layered rare earth hydroxides as drug carriers is still in the initial stage, so it is also of considerable research value to expand the types of drugs carried by layered rare earth hydroxides.

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Notes

The author declares no competing financial interest.

ACKNOWLEDGMENTS

This research was funded by National Natural Science Foundation of China (NSFC, U22B6012, U23B6011)

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