Research Article

Synthesis and Characterization of La-Doped Luminescent Multilayer Films

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In this work, we have successfully designed ordered luminescent multilayer films based on La-doped nonmagnetic or magnetic inorganic nanostructure with electronic microenvironment (EM). The inorganic nanosheets with opposite charge can assemble EM between the interlayers. At the same time, their elements on nanosheets of layer double hydroxides (LDHs) are facile to be replaced so that we can introduce transition metal or lanthanide elements. Besides, ferromagnetic effect (FE) can be formed in this microenvironment due to introducing transition metal on LDHs nanosheets. As a result, we confirm that EM, FE, and doping La element in the LDHs can affect the vibration of backbone of chromophores and then prolong the luminescent lifetime, which suggests a new pathway for developing the novel light-emitting thin films.

1. Introduction

Nowadays, an attractive target has been focused on which is layered materials for both fundamental research and practical application because of their intrinsic unique two-dimensional structure, rich physics, and chemical properties [1–3]. Specifically, the nanosheets of those have been used as structural units in multifunctional construction. Because of the flexibility of composition (nanosheets and guest between interactions), such materials have attracted tremendous attention for their potential applied value [4, 5]. Due to the successful achievement of the monolayer or few nanosheets about layered materials, the layered materials have been serving as functional units to build ordered thin films via layer-by-layer self-assemble method (LBL method) [6–9]. Recently, the scientists assembled successfully ordered and regular multifunctional thin films, such as luminescent films, magnetic films, and even biological films [10–16].

With the urgent targets to deal with the crisis of energy depletion, enthusiastic exploration of the environmental and efficient energy materials are engaged. So luminescent materials based on lanthanide elements have been candidates in order to be applied in optoelectronic devices and optical communications [17, 18]. Series of matrix phosphors doped with various lanthanide ions were obtained and adjusted the element content in order to be applied for white LEDs [19, 20]. A sensitizer was assembled by lanthanide complexes pillaring in inorganic layered materials between the interlayer, and it has attracted tremendous attention for practical device applications [21]. On the other hand, the incorporation of lanthanide ions on the layered materials’ nanosheets has been reported to achieve visible or infrared luminescence, respectively [22].

Layered double hydroxides (LDHs), as a type of significant host-guest materials, have been considered as a fascinating candidate due to their simple preparation method, environmental protection, and excellent chemical stability [23–26]. At the same time, isomorphous replacement of certain M$^{4+}$ cations by M$^{3+}$ cations in LDHs, such as Al$^{3+}$ and Ga$^{3+}$, gives positively charged layers, and montmorillonite’s (MMT) nanosheets also process opposite charge due to different isomorphic substitution compared with LDHs [26, 27]. In our previous work, it was testified that electronic microenvironment (EM) assembled by LDHs and MMT nanosheets can prolong the luminescent lifetimes of thin films [28]. Besides, when introducing transition metal on nanosheets, LDHs can be served as ferromagnetic layers. As a result, we succeeded
in obtaining ordered thin films with ultraprolonged lifetimes and verified that ferromagnetic effect (FE) can also enhance luminescent lifetimes of chromophores in coordination with EM [29]. Herein, in this paper, we synthesized the La-doped magnetic or nonmagnetic LDHs and assembled the luminescent thin films via LBL mthod. By rationally choosing the inorganic nanosheets; we proved that the EM and FE can be beneficial for the optical properties of those luminescent thin films based on La-doped LDHs. Therefore, this work put forward a viable way for fabricating ordered La-doped inorganic nanostructure with EM and FE, which can provide better chance for the application of the next generation of optical devices.

2. Experimental Section

2.1. Reagents and Materials. Mg(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, Co(NO₃)₂·6H₂O, and La(NO₃)₃·6H₂O were all supplied by the Xilong Chemical Plant. NaOH, NH₃·H₂O, H₂O₂ (30%), and H₂SO₄ (95%–98%) were purchased from Beijing Chemical Reagent Company. Bis(N-methylacridinium) (BNMA) was supplied by J&K Scientific, Ltd. Na-montmorillonite (MMT) was supplied by Zhejiang Feng Hong New Materials Co., Ltd., and polyvinyl alcohol (PVA, DP = 1750 ± 50) was manufactured by Tianjin Fuchen Chemical Reagent Plant.

2.2. Characterization. Double beam UV-vis spectrophotometer (TU-1901) was used to monitor the process of the depositing cycles. Fluorescence spectrophotometer (F-4600, Hitachi, Japan) was used to perform the luminescent property deposition cycles. Fluorescence spectrophotometer (F-4600, Hitachi, Japan) was used to perform the luminescent property of the photos. Edinburgh Instruments’ steady and transient time-resolved fluorescence spectrometer was used to test the fluorescence decay, and the 375 nm pulse laser radiation was used as the excitation source.

2.3. Synthesis of La-Doped LDHs. The La-doped LDHs were synthesized via coprecipitation method, similar to our previous work [28]. Typically, divalent metallic cations M²⁺ (Mg²⁺ or Co²⁺) and trivalent metallic cations M³⁺ (Al³⁺ or La³⁺) were mixed in boiled deionized water (M²⁺/M³⁺ = 2 and Al³⁺/La³⁺ = 1). Certain amount of solution of sodium hydroxide was added into the salts solution under ongoing stirring. Mixed solutions were stirred at 80°C for 24 h under N₂ gas, and then the precipitate was centrifuged and dried at 60°C.

2.4. Exfoliation of MgAlLa-LDHs, CoAlLa-LDHs, and MMT. 1 g MMT was added in 1 L deionized water with continuous stirring for 28 d. And then the solution with exfoliated MMT nanosheets was obtained by centrifuging the suspension at 10000 rpm for 10 min. The positively charged MgAlLa-LDHs and CoAlLa-LDHs nanosheets were obtained by 0.1 g MgAlLa-LDHs or CoAlLa-LDHs dispersing in 100 mL formamide and agitating for 48 h.

2.5. Fabrication of Luminescent Thin Films Based on La-Doped LDHs and Luminescent Thin Films Based on La-Doped LDHs and MMT. PVA was dissolved in deionized water at 90°C to form 1 wt% PVA aqueous solution, and then 1 g/L BNMA aqueous solution was mixed with isopyknic PVA aqueous solution to form BNMA@PVA solution.

The quartz slide (3.0 × 1.0 cm²) was cleaned by the mixture of NH₃·H₂O and H₂O₂ solution and then deposited alternatively in MgAlLa-LDHs suspension and BNMA@PVA solution for n cycles to fabricate (MgAlLa-LDHs/BNMA@PVA)n, marked as MgM(n)-films. So do (CoAlLa-LDHs/BNMA@PVA)n, recorded as Co(n)-films. (MMT/BNMA@PVA/MgAlLa-LDHs/BNMA@PVA)n, or (MMT/BNMA@PVA/CoAlLa-LDHs/BNMA@PVA)n, recorded as CoM(n)-films, or (MMT/BNMA@PVA/CoAlLa-LDHs/BNMA@PVA)n, recorded as CoM(n)-films, were obtained by depositing the MMT suspension, BNMA@PVA solution, LDHs suspension, and BNMA@PVA solution in turn, respectively.

3. Results and Discussion

As shown in Figure 1, the intensities of absorption peaks at 265.0 nm and 372.0 nm increase linearly during the layers growth, displaying a stepwise and regular growth procedure. The fluorescence emission intensity also displays a consistent increase at the peak in 515.0 nm with n, as shown in Figure 1(a). The luminescent lifetimes of MgM(n)-films (8.08–8.98 ns) are prolonged by a factor of nearly 2.5 times compared with the pristine BNMA powder (0.37 ns), as shown in Table 1.

This main reason is the rigid structure’s isolation effect (IE), which can stop the aggregation of BNMA. The luminescent lifetimes of MgM(n)-films are prolonged 1.7 times more than those of (CoAlLa-LDHs/BNMA@PVS)n, (4.61–8.88 ns) [18], due to the fact that doping La partially substitutes Al elements.

As seen from Figure 2, two absorbance peaks of MgM(n)-films are at 265.5 nm and 375.0 nm, with stable growth with the layer number (Figure 2, inset). Furthermore, at 520.0 nm, the films have the highest emission band peak and are red-shifted by about 5 nm without any obvious broadening, but the emission intensity also increases regularly with the depositing number. The fluorescence lifetime analysis (Table 1) reveals that the fluorescence lifetime of MgM(n)-films is prolonged by a factor of nearly 30 (10.78–12.11 ns) compared with the pristine BNMA powder (0.37 ns) [18]. Compared with the lifetimes of MgM(n)-films (8.08–8.98 ns), these thin films’ lifetimes are also prolonged about 3 ns. The

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<th>8</th>
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<tr>
<td>𝜏₁</td>
<td>8.553</td>
<td>1.228</td>
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<td>𝜏₂</td>
<td>8.08</td>
<td>8.58</td>
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<td>χ²</td>
<td>2.768</td>
<td>2.501</td>
<td>2.399</td>
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<td>𝜏₁</td>
<td>11.95</td>
<td>2.463</td>
<td>11.51</td>
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<tr>
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<td>11.37</td>
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<td>χ²</td>
<td>3.618</td>
<td>2.138</td>
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first reason is the rigid structure’s IE, stopping the aggregation, and formation of BNMA. But the most important one of all is that EM can be formed by the positive LDHs nanosheets and negative MMT nanosheets, which can affect the vibration of backbone so that it can prolong the lifetimes of the films [28].

At the same time, we selected CoAlLa-LDHs and BNMA to assemble the luminescent thin films via LBL method, in order to generate the FE between the interlayers. Photoluminescence spectra of Co(n)-films (Figure 3) and ordered and uniform enhanced green luminescent thin films are obtained. Owing to CoAlLa-LDHs offering a constant FE, the luminescent lifetimes of Co(n)-films (9.80–10.52 ns) are over 28 times compared to BNMA powder’s lifetimes (0.37 ns) (Table 2), also nearly 3.2 times longer than those of (MgAl-LDHs/BNMA@PVS)n (4.61–4.88 ns), and much larger than thin films based on nonmagnetic MgAl-La-LDHs.

Later, we design the nanoarchitecture with the coexistence of EM and FE to explore the thin films’ optical properties. In Figure 4, the absorption peaks of BNMA
Figure 3: UV-visible absorption spectra and photoluminescence spectra of Co(m)-films. The inset of (a) shows the absorbance increasing linear relationship in 263.5 nm, 338.0 nm, and 375.0 nm.

Figure 4: UV-visible absorption spectra and photoluminescence spectra of CoM(m)-films. The inset of (a) shows the absorbance increasing linear relationship in 263.5 nm, 338.0 nm, and 375.0 nm.

Surprisingly, the luminescent lifetimes of CoM(m)-films (13.67–14.74 ns) are prolonged more than 38-fold than that of BNMA (0.37 ns) and also nearly 4-fold as long as those of (MgAl-LDHs/BNMA@PVS)ₙ (4.61–4.88 ns) (Table 2). Importantly, the luminescent lifetimes of CoM(m)-films are startlingly extended compared with those of MgM(m)-films.
Table 2: Lifetimes of luminescent thin films based on CoAlLa-LDHs. \( \tau_i \) stands for the lifetime of Co(n)-films and \( \tau_f \) stands for the lifetime of CoM(n)-films.

<table>
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<th>( \tau_i/\text{ns} )</th>
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<tr>
<td>( \tau_f/\text{ns} )</td>
<td>9.80</td>
<td>10.30</td>
<td>10.52</td>
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<td>( \chi^2 )</td>
<td>2.107</td>
<td>2.279</td>
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<td>( \tau_f/\text{ns} )</td>
<td>14.02</td>
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<tr>
<td>( \chi^2 )</td>
<td>1.383</td>
<td>1.124</td>
<td>1.208</td>
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Figure 5: The comparison of BNMA’s lifetimes in the different states under different environments. Black dot represents the luminescent lifetime of BNMA powder (0.37 ns), the red dots stand for those of (MgAl-LDHs/BNMA@PVS)\(_n\), and the blue ones show those of Mg(n)-films. The dark green dots stand for those of Co(n)-films. The pink dots stand for those of MgM(n)-films. The green-yellow dots stand for the luminescent lifetimes of CoM(n)-films.

As a result, it is indicated that CoAlLa-LDHs can affect the luminescent property, thus verifying magnetic effect can prolong the lifetimes of chromophores.

Figure 5 illustrates the comparison for luminescent lifetimes of BNMA in different states under different environments. The lifetimes show stepped increase as the different inorganic nanosheets are introduced. When we only design the doped La nonmagnetic LDHs, the lifetime can markedly increase by nearly 2.8-fold. But if we choose the doped La magnetic LDHs, the lifetime can prolong over 3 times. When we successfully assemble EM in the nanostructure, the lifetime can extend by 12.11 ns at most. When introducing La-doped magnetic CoAlLa-LDHs and MMT, the lifetimes reach the highest platform, which obviously confirmed that EM and FE can prolong luminescent lifetimes, synergistically.

4. Conclusions

To sum up, this work successfully assembles the La-doped LDHs and MMT to form EM and designs the cationic chromophores in the rigid microenvironment. Due to the difference of LDHs' components, FE can be introduced in the interlayers. Importantly, it successfully demonstrates that the La-doping, EM, and FE are fairly beneficial to improving the luminescent property. Therefore, it is expected to be potential candidate for manipulating, controlling, and investigating photomagnetoelectric devices.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

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References


[20] Z. Mao, J. Chen, L. Sun, Q. Lu, and D. Wang, "Control of green emitting intermediate phases in (Ba, Sr)\textsubscript{3}MgSi\textsubscript{2}O\textsubscript{8}:Eu\textsuperscript{2+}, Mn\textsuperscript{2+} phosphors for dual-bands or tri-bands emission," Materials Research Bulletin, vol. 70, pp. 908–913, 2015.


