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Layer-by-layer assembly of luminescent ultrathin films by Mg–Al–Eu LDHs nanosheets and organic ligand with high transparency

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ABSTRACT

We fabricated a kind of luminescent ordered multilayer transparent ultrathin films (OMTFs) based on inorganic rare earth doped layered double hydroxides (Mg–Al–Eu LDHs) nanosheets and the organic ligand 2-thenoyltrifluoroacetone (TTA) via layer-by-layer assembly method. At the same time, Polyvinyl Alcohol (PVA) aqueous solution was used as intermediate linkers. UV–visible absorption spectroscopy, X-ray diffraction, fluorescence spectroscopy and scanning electron microscopy were introduced to investigate the structure and properties of these films. Surprisingly, the uniformity and the fluorescence emission intensity of OMTFs which utilized polyvinyl Alcohol (PVA) as intermediate linkers are significantly enhanced compared with that of OMTFs without PVA. Herein, it was found that the fluorescence emission intensity of this kind of ultrathin film with PVA displays a monotonic increase as the number of deposition cycles increasing, and further the films which are highly transparent, uniform and ultrathin have potential applications in the optical display devices.

1. Introduction

In the last few decades, conventional lanthanide organic coordination compounds, especially formed by the coordination between europium or terbium and some ligands, have been the subject of extensive research for their sharp and intense emission bands arising from f–f transition [1]. However, these luminescent materials have the short comings such as poor thermal and optical stabilities and inhomogeneity, which make their application and development seriously restricted. Recently, there are some reports that the luminescence behavior of rare earth contained inorganic–organic hybrids have potential application for light-emitting materials [2,3].

Layered double hydroxides (LDHs) have become increasingly of concern, which can be applied for biosensor [4], the immobilization hosts of functional molecules by intercalation into their layers and fluorescent probe in biology diagnosis [5–8]. By virtue of their intrinsic unique two-dimensional structure [9,10] which can offer a stable environment that enhances the mechanical, thermal and optical stabilities, LDHs have been used as the basic building blocks for making new designed organic–inorganic or inorganic–inorganic nanomaterials [3,8,11,12]. As for LDHs, some groups have just done many profound researches by making use of nanosheets with two-dimensional arrays which can inhibit the aggregation of some substances. From the practical application into consideration, those layered materials having tunable photoluminescent properties such as emission intensity and color have drawn special attentions [13,14]. Duan's group successfully used LDHs nanosheets to assemble photoemissive thin-film which can suppress the chromophores' π–π stacking and thus make organic photofunctional molecules show excellent optical properties [13,15–18]. Liu's team also utilized transition metal-bearing LDHs and montmorillonite (MMT) to assemble a novel luminescent multiple ordered thin-film with ultra-prolonged lifetime [19–21].This is because that the chromophores were confined in the oppositely-charged inorganic layer hosts. Furthermore, combining the advantages of lanthanide ions of high luminescence efficiency with the low excitation energy and high absorption efficiency, rare earth doped LDHs, intercalation LDHs of rare earth complexes and their properties research have been reported [22–25]. However, assembly ultrathin layered film with the rare-earth doped LDHs nanosheets and some kind of organic antenna ligand solution even adding PVA aqueous solution has not been reported in any previous literatures.

In this paper, we report a new type of OMTFs fabricated by use of TTA intercalated into Mg–Al–Eu LDHs with layer-by-layer assembly method (Scheme 1). The structure of PVA molecular chains which contains a lot of polar hydroxyl groups is symmetry and neat, therefore it exhibits remarkable film-forming, excellent solubility in water and biodegradation thoroughly. As the carrier,

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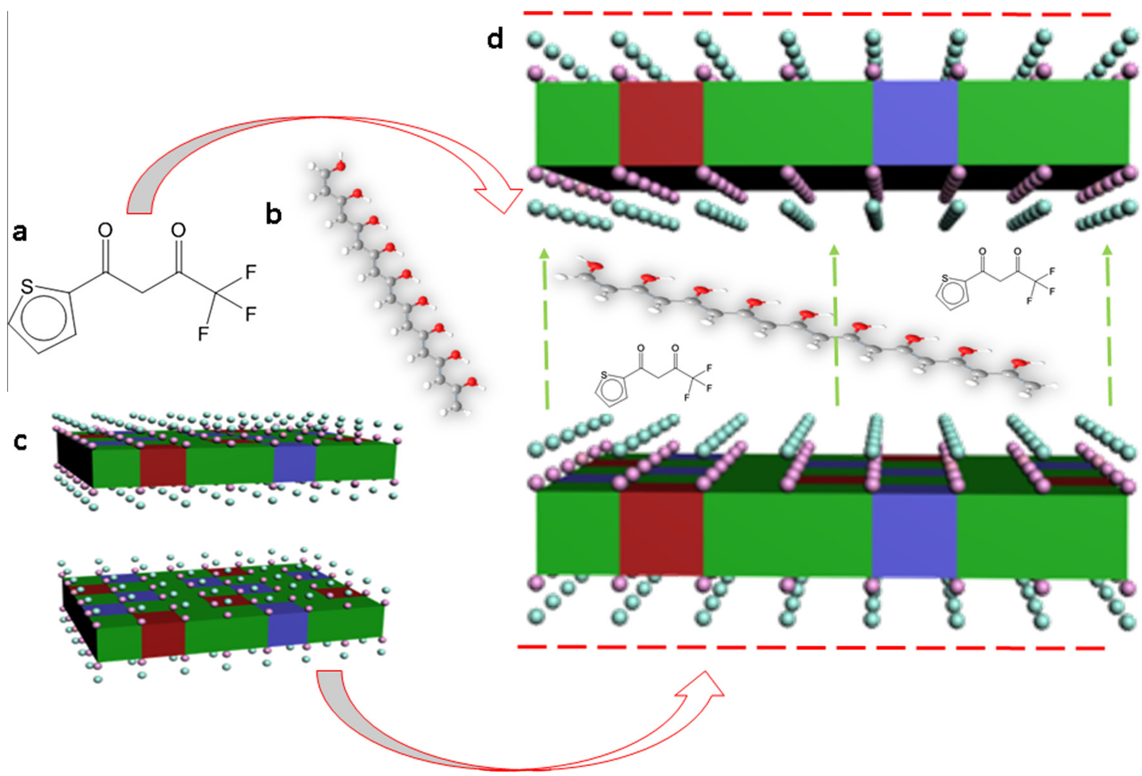

Scheme 1. (a) Structure of TTA; (b) structure of PVA; (c) a representation of Mg–Al–Eu LDHs; (d) the assembly of OMTFs. Blue: aluminum element, dark green: magnesium element, red: europium element.

PVA can make the TTA evenly dispersed. Moreover, PVA can interact with MgAlEu–NO_3 LDHs interlayer water molecule by hydrogen bonding, which prevents hydroxyl stretching vibration causing fluorescence quenching. Thus the fluorescence properties and the uniformity of (Mg–Al–Eu LDHs/TTA)*n* OMTFs formed by the coordination between trivalent europium ion in the layer and TTA were improved. It is also confirmed that the addition of PVA had a remarkable influence on stability and mechanical characteristics of the OMTFs which can emit uniform red light and show a growth of the fluorescence emission intensity upon increasing the number of deposition cycle. Hence, our work successfully developed a simple and facile method to fabricate this sort of inorganic–organic luminescent OMTFs containing rare earth doped LDHs nanosheets.

2. Experimental section

2.1. Materials and Measurements

All the chemicals were of analytical grade and were utilized as received without further purification. TTA and PVA were purchased from Sethjin science and technology development co., Ltd. Mg $(NO_3)_2{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ were all supplied by the Xilong Chemical Plant. $NH_3{\cdot}H_2O$ (25–28%). NaOH, H_2O_2 (30%), H_2SO_4 (95–98%), formamide and anhydrous ethanol were supplied by Tianjin Bot Chemical Corporation. Eu_2O_3 was purchased from Shanghai Yuelong reagent co., Ltd. Deionized water was used in the whole experiment.

Fourier transform infrared (FT-IR) spectroscopy was compiled as KBr disks on Germany Bruker Tensor27 spectrometer in the wavelength range of 4000–400 cm^{-1}. X-ray diffraction (XRD) patterns in the range of 5–90 was recorded using a Germany Bruker AX. UV–visible absorption spectra were conducted in the range of 190 to 800 nm on a TU-1901 Double beam UV–vis spectrophotometer with slit width of 5.0 nm. The morphology of thin-films was examined by using Scanning electron microscopy (SEM S-4800) at a voltage of 3 kV. Edinburgh Instruments model FLS920P spectrometer was used to measure the luminescence spectra and fluorescence lifetime with a 450 W xenon lamp as the excitation source.

2.2. Synthesis of Mg–Al–Eu LDHs

The Mg–Al–Eu LDHs was prepared via hydrothermal coprecipitation method. In brief, 0.230 g Eu_2O_3 powder was dissolved in excess concentrated nitric acid (6 mol L^{-1}). After partly removing the nitric acid by distillation, 7.693 g $Mg(NO_3)_2{\cdot}6H_2O$ and 4.052 g $Al(NO_3)_3{\cdot}9H_2O$ and distilled water were added to form a 60 mL mixed salts solutions. Dilute ammonia (5% $NH_3{\cdot}H_2O$) was dropwise added to the solution under stirring constantly until the pH was adjusted to 10 at 65 °C. Then, the resulting solution was transferred into a stainless autoclave with inner Teflon vessel and hydrothermally reacted at 130 °C for 12 h. After being cooled at ambient temperature, the solid was filtered and washed with distilled water and finally dried in oven at 70 °C for 12 h.

2.3. Exfoliated of Mg–Al–Eu LDHs

The monolayer, positively charged LDHs nanosheets were obtained by vigorously agitating 0.1 g Mg–Al–Eu LDHs in 100 mL formamide at room temperature under an Argon gas flow. After 48 h, the colloidal suspension of exfoliated LDHs nanosheets was obtained after centrifugation at 9000 rpm for 10 min.

2.4. Fabrication of (Mg–Al–Eu LDHs/TTA)n OMTFs

Firstly, the quartz glass slides (2×2 cm^2) were first immersed in the solution ($NH_3{\cdot}H_2O$:H_2O_2 = 7:3) for 60 min and then took it