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Layer-by-layer assembly of luminescent multilayer thin films by MMT, anionic chromophores and magnetic CoAl-LDHs nanosheets

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ABSTRACT

In this report, luminescent multilayer thin films (MTFs) based on oppositely-charged montmorillonite (MMT) and transition metal-bearing layered double hydroxides (LDHs) nanosheets were fabricated via a layer-by-layer assembly method. Oppositely-charged inorganic nanosheets can be expected to assemble an electronic microenvironment (EME), and transition metal-bearing LDHs nanosheets can offer an additional magnetic field (MF) for the chromophores at the same time. Surprisingly, the luminescent lifetimes of MTFs with EME and MF are significantly prolonged compared with that of the pristine chromophores, even much longer than those of MTFs without oppositely-charged and magnetic architecture. Therefore, it is highly expected that the EME and MF formed by oppositely-charged and transition metal-bearing inorganic nanosheets have remarkable influence on enhancing the luminescent lifetimes of chromophores, which suggest a new potential way to manipulate, control and develop the novel light-emitting materials and optical devices at molecular level.

1. Introduction

Layered materials are attractive targets for their rich fundamental physics and potential applications in future multifunctional devices, and the nanosheets of those have been used as building units for making new designed nanomaterials due to their intrinsic unique two-dimensional structure [1–4]. As for LDHs and MMT, several groups have just done many profound researches by using naonosheets with two-dimensional arrays which can provide a rigid and stable environment [5–10]. However, various different inorganic nanosheets possibly have certain natural features, such as LDHs exhibit permanent positive charge and MMT' nanosheets are evolved as permanent negative charge that can be delocalized over the entire layer surface, due to an isomorphic substitution [10,11]. But there was no relational report about taking full advantage of the nanosheets' charge, until our group [12] successfully confirmed that electronic microenvironment, which is assembled by oppositely-charged nanosheets between the interlayer, is fairly beneficial for enhancing the lifetimes of MTFs containing luminescent cations. On the other hand, transition metal-bearing LDHs' nanosheets can act as nanoscale ferromagnetic layers, and their multilayer assemblies exhibit significant magneto-optical response [9,10,13]. And then, our present work confirmed that MF also can improve the optical property in coordination with EME, especially the lifetimes of MTFs [14]. Herein, in this paper, what we are most interested in are whether anionic luminescent polymers can be designed for intercalating into EME and MF environments, and whether they can be affected by the different ferromagnetic inorganic nanosheets on the optical properties.

In this work, a luminescent π-conjugated anionic polymer poly [5-methoxy-2-(3-sulfopropoxy)-1,4-phenylenevinylene] potassium (APPV) was assembled with the CoAl-LDHs nanosheets and MMT nanosheets to fabricate multilayer thin films (MTFs), respectively. In the nano-system, as the assembled nano-architecture can provide an EME and the CoAl-LDHs can offer a constant MF to the chromophores (Fig. 1), the MTFs exhibit remarkable optical properties with reasonably longer luminescent lifetimes. Herein, this work successfully fabricates the MTFs with EME and MF′, which can promote the hybrid systems with various functions, and confirm the concept about the EME and MF effecting chromophores simultaneously.

2. Results and discussion

We selected the luminescent π-conjugated anionic polymer to assemble with different ferromagnetic inorganic nanosheets, in order to confirm the universality of the novel concept about EME and MF effecting the more series chromophores. The UV–visible absorption spectra of $(\text{CoAl-LDHs/APPV@PVA})_n$ MTFs with varying numbers of assembly steps are shown in Fig. 2a, and the intensity of absorption

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peaks exhibit correlate linearly with the deposition cycles (Fig. 2a, inset), demonstrating a stepwise and regular growth procedure. Furthermore, the fluorescence emission intensity also displays a consistent increase with the layer growing, as shown in Fig. 2b. This can also be visualized by irradiating MTFs under daylight and UV light (365 nm), respectively (Fig. 2c), where these films exhibit uniform enhanced luminescence with increasing number of deposition cycles. Above all, the MTFs exhibit an ordered and regular film growth procedure and uniformly enhanced yellow luminescence as the layer number increases.

Wondrously, it is remarkable that the luminescent lifetimes of (CoAl-LDHs/APPV@PVA)$_n$ MTFs (1.30–1.44 ns) are more than 2 times as long as the pristine APPV solution (0.6 ns) (Fig. 2d), and are also nearly 2 times the length of (MgAl-LDHs/APPV)$_n$ MTFs (0.66–0.81 ns) [7]. The profound increasing is partially due to the positive-charged CoAl-LDHs nanosheets' electrostatic attraction and isolation effect, preventing the formation of APPV aggregation. But most importantly, CoAl-LDHs can offer a constant MF, thus apparently affecting the vibration of the valence electron of the chromophores which will definitely prolong their lifetimes. According to this remarkable increase, it is confirmed that MF can definitely prolong anionic chromophores' lifetimes.

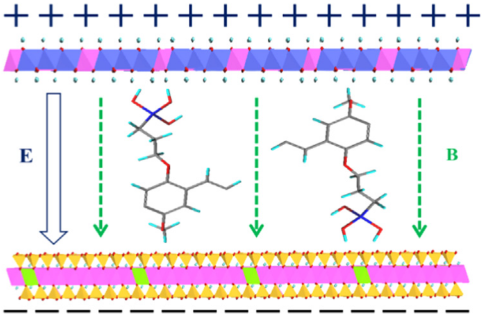

Fig. 1. Schematic of APPV in EME and MF between the MMT and CoAl-LDHs nanosheets.

At the same time, in order to verify the EME being able to affect the luminescent lifetimes of anionic chromophores, (MMT/APPV@PVA/CoAl-LDHs/APPV@PVA)$_n$ MTFs were also fabricated via the same layer-by-layer assembly method. In accordance with UV–visible absorption spectra, photoluminescence spectra and the photos under daylight and UV light (365 nm) of (MMT/APPV@PVA/CoAl-LDHs/APPV@PVA)$_n$ MTFs (Fig. 3a–c), MTFs, which exhibit ordered and regular enhanced yellow luminescent as the layer number increases, are obtained.

Surprisingly, it is amazing that the luminescent lifetimes of (MMT/APPV@PVA/CoAl-LDHs/APPV@PVA)$_n$ MTFs (1.75–1.86 ns) are prolonged more than 2.5-fold compared with the (MgAl-LDHs/APPV)$_n$ MTFs (0.66–0.81 ns), and are also amazingly prolonged 3-fold compared with the pristine APPV solution (0.60 ns) (Fig. 3d) [7]. Importantly, the luminescent lifetimes of (MMT/APPV@PVA/CoAl-LDHs/APPV@PVA)$_n$ MTFs are startlingly extended to about 1.3-fold compared with those of (CoAl-LDHs/APPV@PVA)$_n$ MTFs. Above all, EME is benefitted for the luminescent lifetimes of anionic chromophores.

According to this remarkable increase, the theory, as mentioned above, that EME and MF can definitely prolong chromophores'

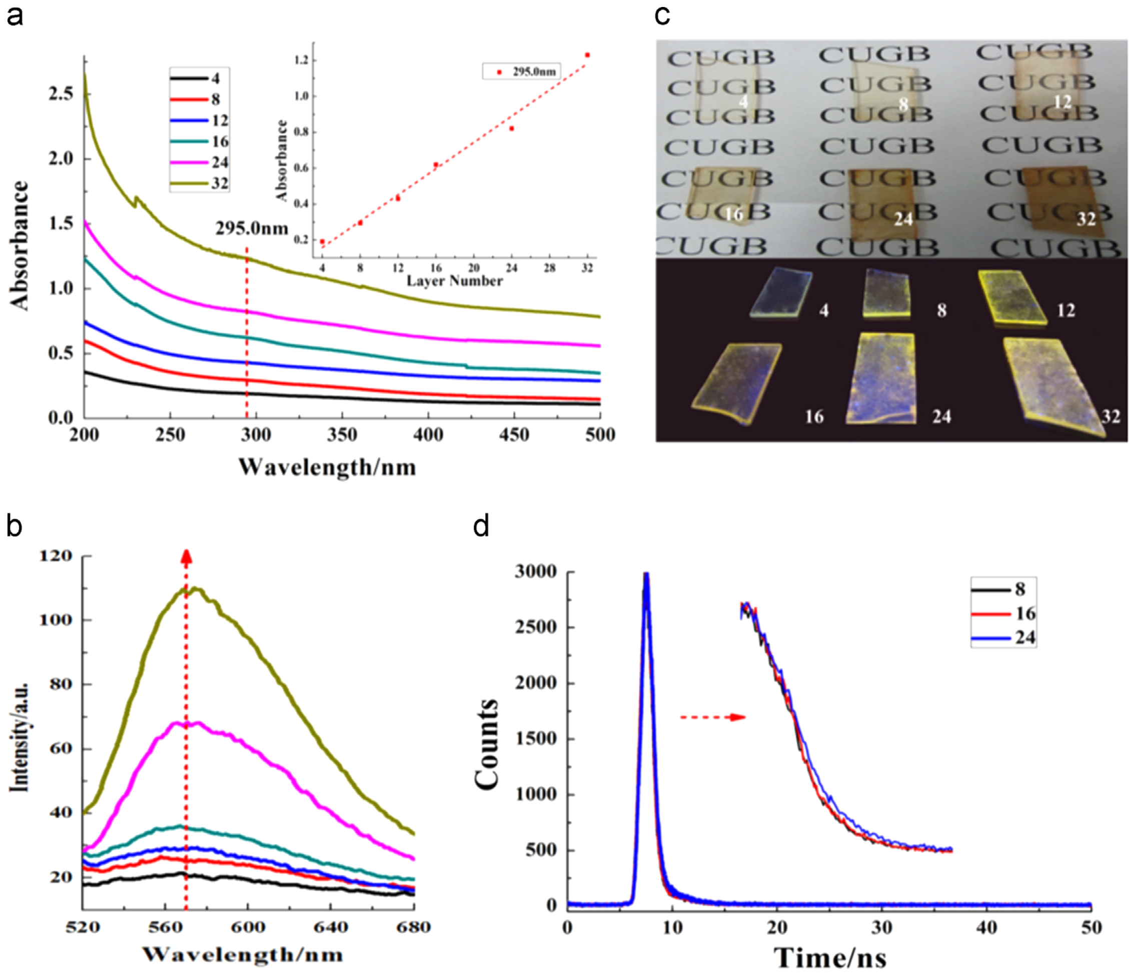

Fig. 2. Characterization of (CoAl-LDHs/APPV@PVA)$_n$ MTFs (a) UV–visible absorption spectra, the inset shows the absorbance increasing linear relationship in 295.0 nm. (b) Photoluminescence spectra. (c) Photographs of MTFs with different layer numbers under daylight and UV light, respectively. (d) Fluorescence decay profiles.