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Fluorescence of Mg-Al-Eu Ternary Layered Double Hydroxide Sensitivity to Phenylalanine

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Abstract We reported for the first time the fluorescence sensitivity of a Mg-Al-Eu ternary layered double hydroxide (LDH) to phenylalanine (Phe). As shown in fluorescent spectra, the red emissions resulted from $^5D_0$-^7F_J transition (J=1, 2) of Eu^{3+} were quenched by Phe, and a strong peak around at 492 nm emerged. A strong interaction between the Mg-Al-Eu LDH and Phe was manifested by markedly different chemical shift positions of the Mg 2p, Al 2p, Eu 4d, O 1 s, and C 1 s peaks in the XPS spectra from those of the LDHs. These results showed that the charges transfer from Phe to the trivalent Eu ions may be taken place.

Keywords Fluorescence · Eu^{3+} emission · Sensitivity ·
Mg-Al-Eu LDH · Phenylalanine

Introduction

Studies on the intercalation of amino acids into layered double hydroxides (LDHs), usually into Zn/Al- and Mg/Al-LDH, were extensively carried out because of their potential applications in drug delivery system [1–5], drug reservoir [6, 7], biosensor [8–10], treatment of industrial wastewaters [11], etc. The application of LDHs relative to biosensors was based on a response to electricity. For examples, Li et al. prepared Ni-Al-LDH

nanosheet film used as the working electrode of a nonenzymatic glucose sensor [8]. Mousty et al. developed the AlP/MgAl−LDH biosensors for enzyme [9]. Ni-based LDH as the supporting matrix of enzymes was studied as an electrochemical biosensor [10]. In this paper, we have studied the Mg-Al-Eu ternary LDH sensitivity to an amino acid, as was scarcely reported; and a LDH-biosensor based on a response to visible luminescence should be meaningful.

Anionic Eu(III) complexes, such as EuL_1 (L_1=tris (dipicolinate)) [12], $[Eu(PW_{11}O_{39})_2]^{11-}$[13], and [Eu (EDTA)(H_2O)_3]$^-$ [14], were intercalated in the interlayer of ZnAl-LDHs, and the luminescence of the Eu (III) complexes was affected by the ZnAl-LDHs. Zhuravleva et al. found that the intensity ratio of $^5D_0 \rightarrow {}^7F_2$ to $^5D_0 \rightarrow {}^7F_1$ transitions resulted from Eu(III) complex intercalated in the interlayer of MgAl-LDH considerably increased with a decreased in the charges of the Layer of MgAl-LDH [15]. However, the Eu^{3+} ions incorporated in the layers of LDHs should be paid attention since the Eu^{3+} ions inside the layers were more easily touched by exoteric substance. This way is favorable for application in fluorescent bioprobe. Accordingly, we have ever synthesized the Mg-Al-Eu ternary LDH and found it was possessed of characteristic red emissions resulted from the $^5D_0$–^7F_j (j=1, 2, 3, 4) transition of Eu^{3+} ions in views of the cheap material and actual application [16]. Then we continued to investigate the fluorescence of the ternary LDH sensitivity to the Phenylalanine in the present paper. As described in the article, the red emissions attributed to the Mg-Al-Eu LDH were almost quenched by the phenylalanine (Phe), which is an important property used in fluorescent bioprobes. For example, the property that the fluorescence of Mg-Al-Eu LDH sensitivity to amino acids can be used to probe the structural changes of DNA because the amino acids are the

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important components of DNA. The Mg-Al-Eu LDH biomaterial with layered structure may be higher thermal stability and less toxicity than those biological organic materials, and larger surface area (excellent adsorption) than other structural bulk materials.

Experimental detail

Synthesis

$MgCl_2$, $AlCl_3 \cdot 6H_2O$, Eu_2O_3, $NH_3 \cdot H_2O$, and HCl were of A. R. grade, and were purchased from Chemistry Reagent Corporation of National Medicine Group. Mg-Al-Eu ternary LDH, with the molar ratios of Mg/(Al+Eu) of 2 and Eu/(Al+ Eu) of 0.06, was synthesized by the coprecipitation method previously reported [16]. CO_2-free deionized water was used in the synthesis procedure. The procedure was followed as: $NH_3 \cdot H_2O$ solution was gradually added to the mixed solutions of $MgCl_2$, $AlCl_3$, and $EuCl_3$ with certain molar ratios, and continuously stirring. After precipitation (pH≈8), the slurry was filtrated, washed with CO_2-free deionize water, and dried at 90 °C for 6 h.

The product (0.782 g) was added into a sodium phenylalanine aqueous solution (200 mL, 0.16 M, pH≈ 10), and kept under magnetic stirring at room temperature for a week. The resulting solid was filtered, water-washed, and dried at 90 °C for 12 h.

Characterization

Chemical contents of Mg, Al, and Eu were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, OPTIMA 5300DV, AMERICAN PE COMPANY). X-Ray powder diffraction (XRD) patterns were recorded on a Bruker D8 Focus (40 kV, 40 mA) with Cu-K_α radiation. The XRD patterns of all the samples were measured with step size of 0.02°, scanning rate of 2°/min, and 2θ ranging from 4.0 to 70°. The Fourier Infrared spectra (FTIR) of the samples were obtained with Shimadzu IR Prestige-21 FTIR spectrometer by the KBr method.

The X-Ray photoelectron spectroscopy (XPS) was performed with a Thermo ESCALAB 250 (V.G. Scientific Co. UK) using monochromatic Al Kα radiation (1486.6 ev) as the excitation source. All spectra were acquired at a pass energy of 20 eV with the anode operated at 150 W. Scanning electron microscope (SEM) observation was carried out using XL 30 ESEM FEG (PHILIPS) operated at 20.00 kV.

The fluorescence of the samples was studied with the help of F-4600 FL spectrophotometer. All measurements for characterization were performed at room temperature.

Results and discussions

Fluorescence

The LDH, Phe and composite were subjected to measurement for the photoluminescence (PL) in the range 440–720 nm under excitation at 380 nm. As shown in Fig. 1 for the LDH sample, two strong red emissions at 594 and 618 nm, attributed to the transitions $^5D_0-^7F_1$ and $^5D_0-^7F_2$ of Eu^{3+} ions, respectively, were observed [17–19]. It is well known that the intensity of the $^5D_0-^7F_1$ transition allowed by the magnetic dipole mechanism is not much influenced by the chemical environment; and the $^5D_0 \rightarrow ^7F_2$ is a typical electric dipole transition and hypersensitive to the chemical environment around the Eu^{3+} ions, giving valuable information of anions coordinating the Eu^{3+} ion [20]. No fluorescence occurred in the measured wavelength range for the pure
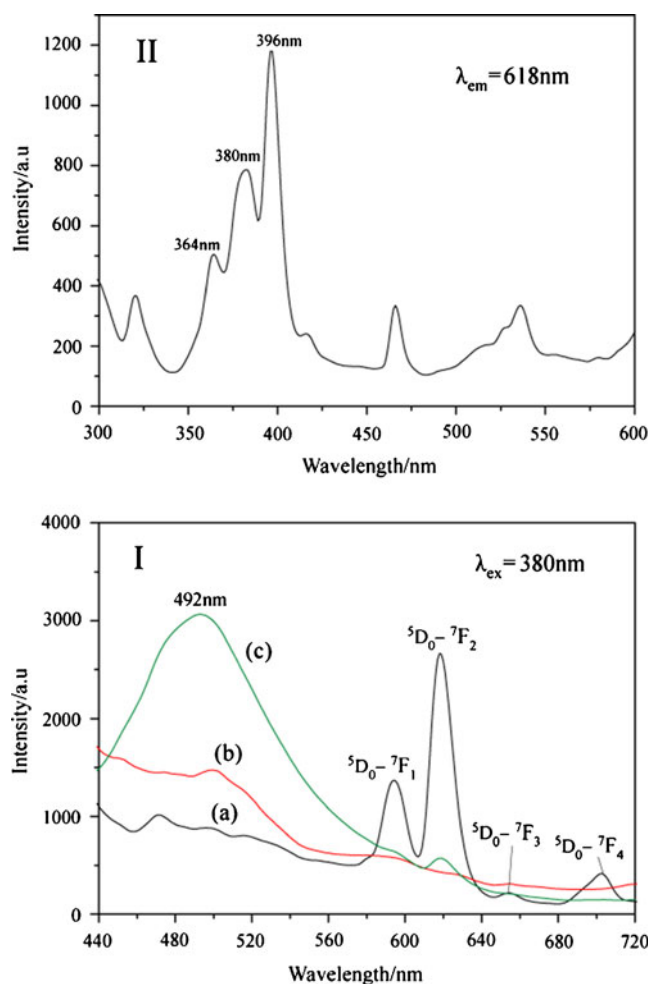

Fig. 1 Emission spectra (I) of (**a**) Mg-Al-Eu LDH, (**b**) Phe, and (**c**) Mg-Al-Eu/Phe- composite (λ_{ex}=380 nm) and the excitation spectrum (II) of the Mg-Al-Eu LDH (λ_{em}=618 nm)
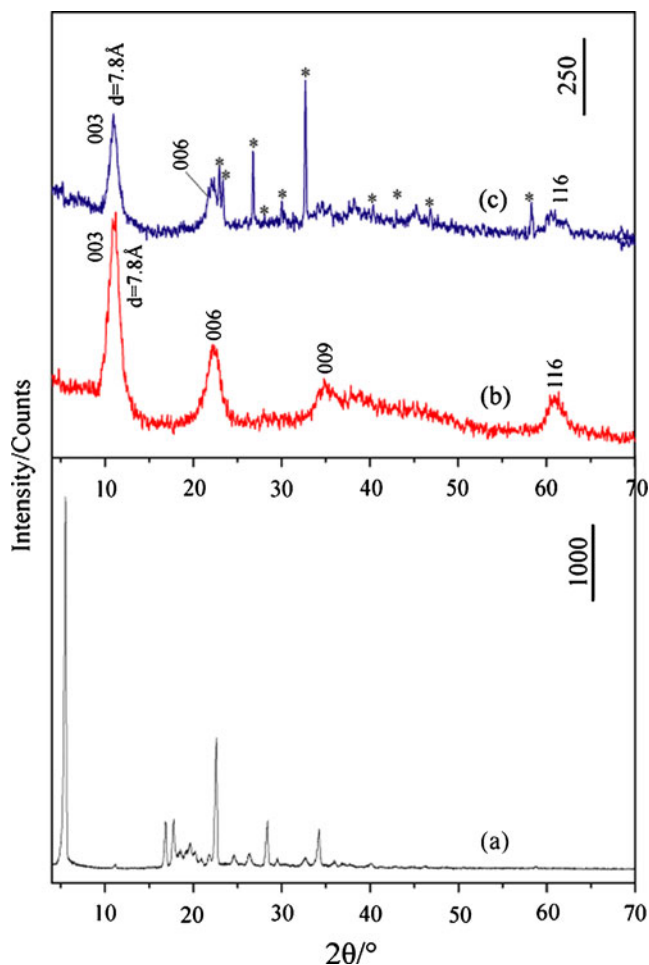
Compositional and structural analysis

The formula of the Mg-Al-Eu LDH was estimated to be $Mg_2Al_{0.94}Eu_{0.06}(OH)_6Cl \cdot 1.36H_2O$ by ICP and TG analysis [16], in which only the chloride was considered as compensating anion and the presence of small carbonate impurities in the interlayer space was not taken into account in the chemical formula. ICP and CHN element analyses indicated that the Mg-Al-Eu/Phe-composite had molar ratio of Phe to Mg-Al-Eu LDH to be 0.4/1. The fluorescent change in the Mg-Al-Eu LDH as Phe was introduced indicated the chemical interaction between the Mg-Al-Eu LDH and Phe. Although Phe was not intercalated into the interlayer of LDH as shown in the XRD patterns (seen in Fig. 2), where the basal spacing of the ternary LDH, 7.8Å, was not noticeably changed, and some reflections (signed as *) due to Phe were observed in the XRD pattern of the Mg-Al-Eu/Phe composite (shown in Fig. 2c). This indicated that the Phe may be chemically absorbed on the layers of ternary LDH, which should be more favorable for application in fluorescent bioprobe.
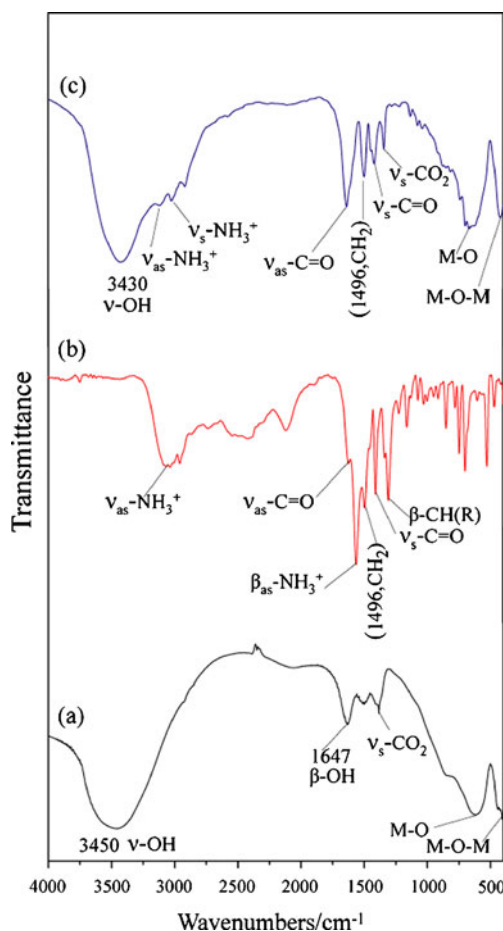

Fig. 2 XRD patterns of (**a**) Phe, (**b**) Mg-Al-Eu LDH, and (**c**) Mg-Al-Eu/Phe-composite, respectively

Phe powder, whereas for the Mg-Al-Eu/Phe-composite, the red emissions due to the transitions $^5D_0 - ^7F_J$ (J=1, 2, 3, 4) of Eu^{3+} were quenched and a strong blue emission around at 492 nm produced. The quenching of fluorescence was often caused by such factors as temperature [21], introduced other ions [22], and introduced ligands [23], etc. The present change of fluorescence may be ascribed to the ligand-to-metal charge-transfer [24]. This change is not yet clearly understood and needs to be further investigated in connection with intensive investigations on the interaction between Mg-Al-Eu LDH and Phe. The excitation spectrum (seen in Fig. 1II) was monitored for the red $^5D_0 - ^7F_2$ emission (λ_{em}=618 nm) of Eu^{3+} ions in the Mg-Al-Eu LDH. According to the excitation spectrum, the favorable excitation wavelengths for the red $^5D_0 - ^7F_2$ emission of Eu^{3+} ion were at 364, 380 and 396 nm, and the optimal excitation wavelength at 396 nm. We selected the excitation wavelength at 380 nm for all the samples in consideration of the blue emission at 492 nm for the Mg-Al-Eu/Phe-composite.

Fig. 3 FT-IR spectra of (**a**) Mg-Al-Eu LDH, (**b**) Phe, and (**c**) Mg-Al-Eu/Phe-composite, respectively. (ν, stretching; β, bending; s, symmetric; as, asymmetric)

IR spectra, XPS and SEM images

The IR spectra of Mg-Al-Eu LDH and Mg-Al-Eu/Phe composite were shown in Fig. 3. The bands around at 3450 (or 3430cm^{-1}) and 1647cm^{-1} were assigned to O–H stretching and bending vibrations of the hydroxide basal layer or interlayer water molecule for the LDH and composite [25]. The band of amine N–H stretch around at 3050 cm^{-1}, and the bands of R-COO^{-} antisymmetric and symmetric stretches around at 1623 and 1410 cm^{-1}, respectively, were observed for the Phe and composite [26, 27]. The vibrational modes of the lattice resulted from the M–O and O–M–O bonds around at 645 and 430cm^{-1} are found in the LDH and composite [28]. It was noteworthiness that the bands attributed to ν_{as}-NH$_3^+$ and β_{as}-NH$_3^+$ seen in the pure powders decreased markedly and even
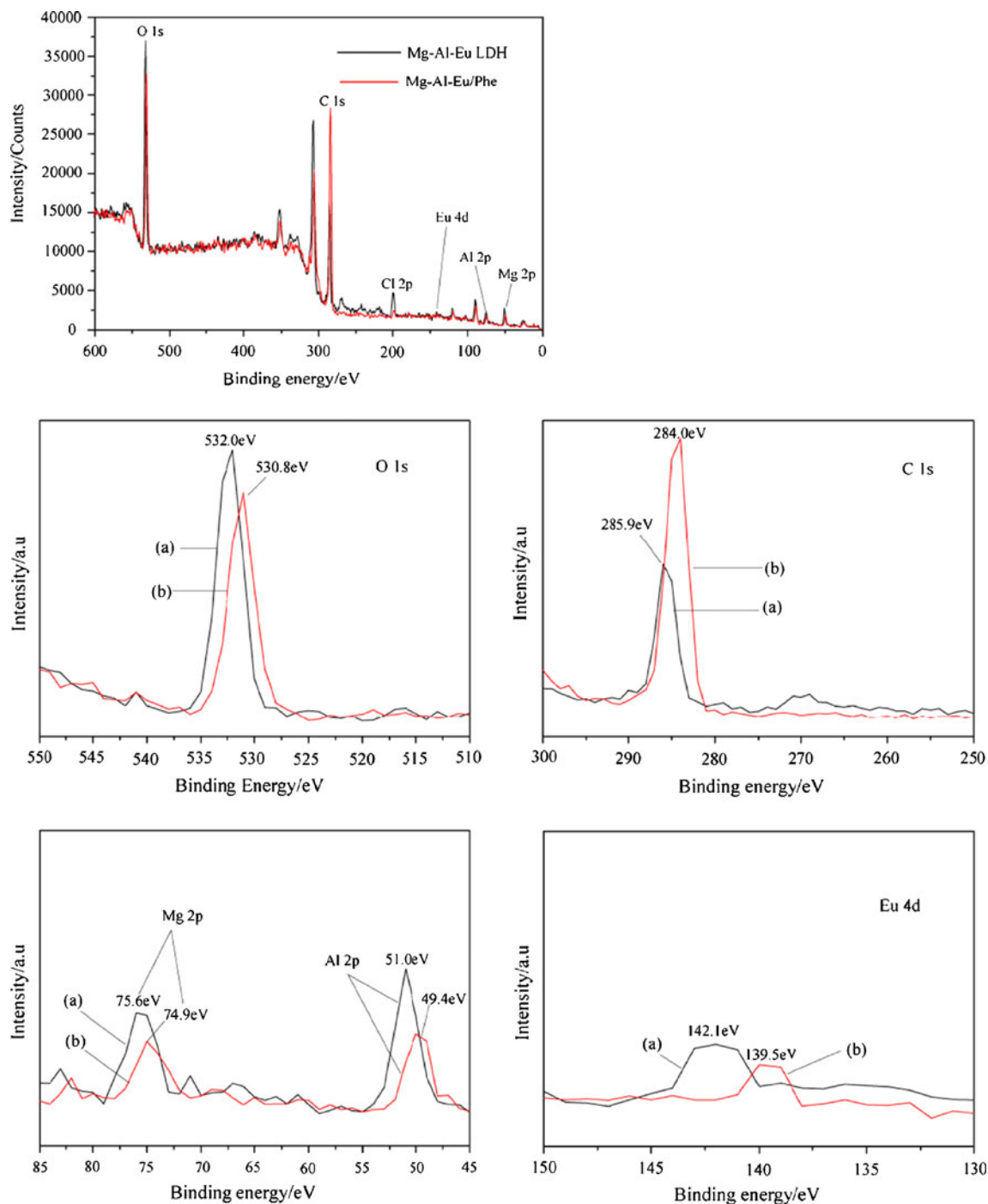

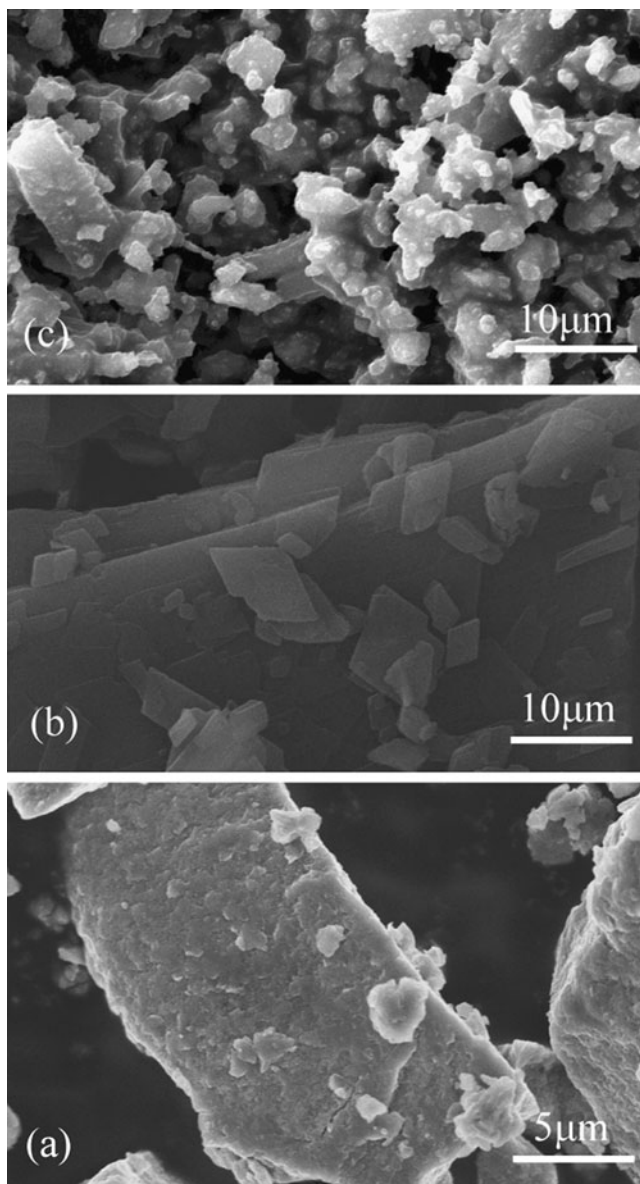Fig. 4 XPS survey spectra of (a) Mg-Al-Eu LDH and (b) Mg-Al-Eu/Phe-composite

Fig. 5 SEM images of (**a**) Mg-Al-Eu ternary LDH, (**b**) Phe, and (**c**) Mg-Al-Eu/Phe-composite, respectively

vanished in the Mg-Al-Eu/Phe-composite. This suggested that the N atom may be interacted with the metal ions in the layers of LDH. However, the evidence of the interaction was further supported by the XPS survey spectra (shown in Fig. 4), where the chemical shift positions of the Mg 2p, Al 2p, Eu 4d, O 1 s, and C 1 s peaks for the Mg-Al-Eu/Phe composite changed obviously compared with that of the Mg-Al-Eu LDH. Moreover, SEM images (Fig. 5) also showed that the shape of the Mg-Al-Eu/Phe-composite was obviously different from that of the Mg-Al-Eu LDH and Phe. All the results indicated chemical interaction occurring between the Mg-Al-Eu LDH and Phe.

Conclusion

In conclusion, the Mg-Al-Eu/Phe composite was obtained. The red emissions due to the transitions $^5D_0–^7F_J$ (J=1, 2, 3, 4) of Eu^{3+} incorporated in LDH were quenched and a strong blue emission around at 492 nm emerged as the Phe was introduced. The chemical interaction may took place between the Mg-Al-Eu LDH and Phe. The sensitivity of fluorescence to Phe makes the Mg-Al-Eu LDH material potential application in biological probe. This material should be more high thermal stability and less toxicity compared with those organic materials used in biological probe.

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