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Eu(III) doped LDH intercalated with cinnamate anion as multifunctional sunscreens

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ABSTRACT

Eu(III) doped Zn_2Al-LDH intercalated with cinnamate anions with different $C_9H_7O_2^-/M^{3+}$ molar ratios were synthesized by different anion-exchange methods. The XRD patterns indicate the formation of hydrotalcite-like compounds. UV–VIS absorption spectra show that the hybrid materials obtained have UV shielding capacity. PLS measurements show low-intensity red light emission of the characteristic europium and cinnamate ions that is recommended to induce collagen production.

1. Introduction

The excessive exposure to solar radiation causes sunburns, irregular skin pigmentation, premature aging, immune system function modifications and skin cancer [1]. Therefore, sun protection is essential to our physical and mental well-being. The necessity to protect people´s skins from the harms caused by sun radiation has significantly promoted the development of materials with great UV radiation protection, high photochemical stability and low toxicity, i.e., new sunscreens [2,3]. Depending on the sunscreen composition, besides UV protection, this type of material may achieve other beneficial functions to the organism such inducing collagen production. Collagen is the main fibrillar protein responsible for the skin's viscoelastic properties and its biosynthesis by fibroblasts is induced by the incidence of low-intensity radiation in the spectral region of 580–700 nm [4,5], which also includes the red-light.

Multifunctional sunscreens may be obtained by doping inorganic host matrices with metal ions and/or by intercalating ionic species into them, such as layered double hydroxides (LDH). The LDH, also known as hydrotalcite-like compounds or anionic clays, have two-dimensional structures organized with flexible pores. These materials are capable of having negative species intercalated in the interlayer region in order to neutralize the positive charges of the layers. Thus, the species inserted in the interlayer spacing acquire extra stability through electrostatic interactions [6]. In general, LDH present themselves as having the following formula $[M^{2+}_{(1\text{-}x)}M^{3+}_x(OH)_2](A^{n-})_{x/n}.zH_2O$ (M = metal ions and A^{n-} = interlayer anion) and a structure derived from brucite mineral [7]. The intercalation of chromophore species in LDH has been widely reported in the literature [8–10] due to the broad-spectrum sunscreens that were obtained having low toxicity and high chemical, thermal and/or photochemical stability. Besides, LDH doped with metal ions, especially lanthanide ions presenting luminescent properties, have been the subject of studies in recent scientific publications [11–13]. The growing interest in LDH doping is related to future 2D applications of these materials in several areas [7].

In this perspective, the Eu^{3+} ion, which has an intense red-light emission and is used as a spectroscopic probe for the determination of local structures [14] due its intraconfigurational 4–4 f transitions, can be highlighted. Moreover, the red-light emission of the Eu^{3+} ion can be improved by inserting a sensitizer into the compound of interest, which then performs the energy transfer process. The energy transfer is suitable if there is an interaction between both chemical entities [15]. Therefore, the study of intercalating chromophore species in the LDH doped with Eu^{3+} ions is of great significance for the development of new multifunctional sunscreens. Thus, this work aims to investigate potential multifunctional sunscreens obtained by the interaction of 3-phenyl-2-propenoic acid (cinnamic acid) sunscreen, in its anionic form, in the Zn_2Al-LDH matrix doped with Eu^{3+} ions to emphasize the materials spectroscopic characterization.

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2. Experimental

2.1. Sample preparation

Zinc chloride ($ZnCl_2$ – 99.98%, Vetec), aluminum chloride hexahydrate ($AlCl_3{\cdot}6H_2O$ – 99.98%, Synth), Europium oxide (Eu_2O_3 – 99.99%, CSTARM), cinnamic acid ($C_9H_8O_2$ – 99.99%, Sigma-Aldrich), hydrochloric acid (HCl – 99.98%, Qhemis) and sodium hydroxide (NaOH – 98.67%, Synth) were used without further purification. The europium chloride ($EuCl_3$) solution was prepared by dissolving the solid Eu_2O_3 in a hydrochloric acid solution; the sodium cinnamate salt ($NaC_9H_7O_2$) was obtained by mixing $C_9H_8O_2$ and NaOH, at a 1:1 molar ratio, in a mixed solution of ethanol and water. LDH were synthesized by the coprecipitation method at constant pH [16]. A mixed solution of zinc, aluminum (Zn^{2+}/Al^{3+} molar ratio equal to 2) and europium chloride (1.0 mol% of Eu^{3+}), in the case where Eu^{3+} substitutes for Al^{3+}, was added slowly and under stirring to 150 mL of deionized water at room temperature and nitrogen atmosphere. The solution pH was adjusted to 6.5 by the addition of a 0.2 mol L^{-1} solution of NaOH. The suspension was kept under stirring for 3 h in nitrogen atmosphere. The solid obtained was filtered, washed with deionized water and dried at room temperature for 24 h. For the preparation of hybrid materials, the doped LDH was added in a solution of sodium cinnamate salt ($C_9H_7O_2^-/M^{3+}$ molar ratio equal to 5 or 7) and the suspension obtained was subjected to hydrothermal treatment for 24 h at 100 °C or to stirring for 14 days at room temperature. The solids were filtered, washed with deionized water and ethanol and dried at room temperature for 24 h. The hybrid material obtained by stirring with $C_9H_7O_2^-/M^{3+}$ = 7 molar ratio was designated $Zn_2Al_{1-x}Eu_x$-Cnm$_7$-LDH/S and hybrids obtained by hydrothermal treatment with $C_9H_7O_2^-/M^{3+}$ = 5 or 7 molar ratios were designated as $Zn_2Al_{1-x}Eu_x$-Cnm$_5$-LDH/HT and $Zn_2Al_{1-x}Eu_x$-Cnm$_7$-LDH/HT, respectively.

2.2. Characterization techniques

X-ray diffraction (XRD) patterns of powdered samples were recorded on a Rigaku diffractometer, model RINT 2000, using CuKα radiation (1.5418 Å, 40 kV, 70 mA, scan 2θ range 3–70° and scan speed 0.02°/10 s) and Ni filter. FTIR spectra were collected in the 4000–368 cm^{-1} region in a Bruker spectrophotometer, model FTIR-Vertex70, using the ATR method. Diffuse reflectance spectra of powdered samples were recorded on a Perkin Elmer spectrophotometer, model LAMBDA 1050 UV–VIS–NIR, equipped with Spectralon 150 nm integrating sphere. Color index was obtained in a Konica Minolta spectrophotometer, model CM-2500d, equipped with d/8° integrating sphere (CIELab color space). The emission and excitation spectra were recorded in a Fluorolog Horiba Jobin Yvon spectrophotometer, model FL3–222, using a continuous xenon lamp irradiation source (450 W) and a Hamamatsu R928 photomultiplier. Molecular modeling of the cinnamate anion was performed by semi-empirical calculations in the MOPAC2016 software, using the Sparkle/RM1 model with the keywords: BFGS, XYZ, SPARKLE, RM1, GNORM = 0.25, PRECISE and CHARGE = −1 (see Table S1 and Fig. S1 in the Supplementary Material).

3. Results and discussion

3.1. Structural analysis

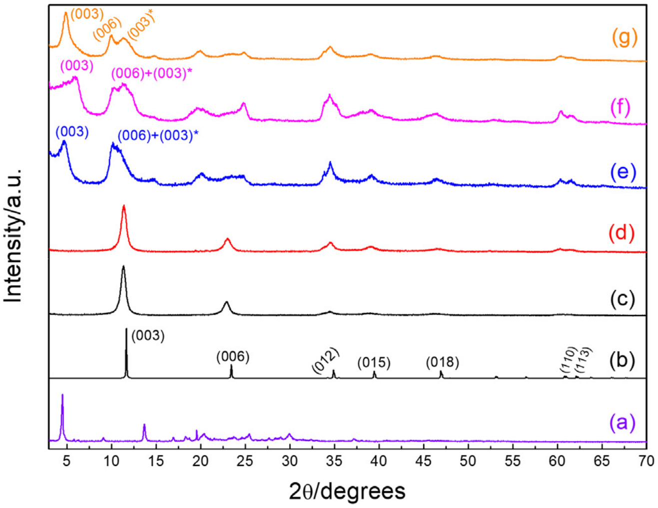

Fig. 1. XRD patterns of (a) sodium cinnamate salt, (b) JCPDS-PDF-89–460 card, (c) Zn_2Al-Cl-LDH, (d) $Zn_2Al_{1-x}Eu_x$-Cl-LDH, (e) $Zn_2Al_{1-x}Eu_x$-Cnm$_5$-LDH/HT, (f) $Zn_2Al_{1-x}Eu_x$-Cnm$_7$-LDH/HT and (g) $Zn_2Al_{1-x}Eu_x$-Cnm$_7$-LDH/S.

Comparing the XRD patterns of samples (Fig. 1) with the JCPDS-PDF-89–460 card corresponding to hydrotalcite-like compound (rhombohedral unit cell and space group *R*3*m*) and also comparing them to a series of layered double hydroxides described in the literature [17], it is observed the LDH formation have good structural organization and phase purity. In the XRD patterns of the LDH, the diffraction peaks situated above 30°/2θ are assigned to brucite-like layer structures, while the harmonic reflections (00l) located in low-angle 2θ region are attributed to layer stacking, which is directly associated to intercalated anions [18]. Thus, basal spacing is calculated from the interplanar distances (d_{hkl}) of the respective basal reflections. So, *a* parameter is equal to interplanar distance d_{110} multiplied by 2 and *c* parameter is defined as interplanar distance d_{003} multiplied by 3 for the LDH compounds with rhombohedral symmetry *R*3*m* such as the layered materials obtained above [17].

Analyzing the d_{003} values of Zn_2Al-Cl-LDH and $Zn_2Al_{1-x}Eu_x$-Cl-LDH (Table 1) against the values reported in literature [19], it is observed that the anion in greater quantity in the interlayer region is the chloride ion, which has d_{003} close to 7.8 Å. The presence of chloride ions inside the interlayer space facilitates the intercalation the anion of interest, especially by using the method of synthesis described above to obtain the hybrid materials, because chloride anions have a low capacity of stack assembly when compared to other anions, mainly the carbonate ion [19].

For the $Zn_2Al_{1-x}Eu_x$-Cl-LDH sample, detailed modifications in the *a* and *c* parameters are observed (Table 1). Those parameters refer to the distances between cations of the LDH layers and the distances between three consecutive layers, respectively. Modifications among them are associated with point distortions of the LDH crystalline lattice caused by the insertion of small quantities of the Eu^{3+} ion [11]. The XRD

Table 1
Interplanar distances d_{003} and d_{110}, lattice parameters (*a* and *c*), basal and interlayer spacing of samples.

Sample	**d_{003}**	**d_{110}**	***a* /Å**	***c* /Å**	**Basal spacing /Å**	**Interlayer spacing[b] /Å**
Zn_2Al-Cl-LDH	7.80	1.54	3.08	23.40	7.77	2.97
$Zn_2Al_{1-x}Eu_x$-Cl-LDH	7.76	1.53	3.06	23.28	7.75	2.95
$Zn_2Al_{1-x}Eu_x$-Cnm$_5$-LDH/HT	18.56 8.72[a]	1.54	3.08	55.68 26.16[a]	17.92 8.18[a]	13.12 3.38[a]
$Zn_2Al_{1-x}Eu_x$-Cnm$_7$-LDH/HT	15.24 7.71[a]	1.53	3.06	45.72 23.13[a]	15.33 7.73[a]	10.53 2.93[a]
$Zn_2Al_{1-x}Eu_x$-Cnm$_7$-LDH/S	18.26 7.76[a]	1.54	3.08	54.78 23.28[a]	17.95 7.68[a]	13.15 2.88[a]

[a] LDH intercalated with chloride ions.

[b] Interlayer spacing corresponds to the difference between basal spacing and brucite-like sheet thickness (4.8 Å).