




Preparation, intercalation, and characterization of nanostructured (Zn, Al) layered double hydroxides (LDHs)

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The term layered double hydroxides (LDHs) is used to define synthetic or natural lamellar hydroxides with 2 or more kinds of metallic cations in the main layers, and hydrated interlayer domains, containing anionic species. Layered double hydroxides, also known as hydrotalcite materials, have attracted considerable interest from both industry and academia. They are interesting for their intercalation properties as they are capable of accommodating complex organic molecules. Therefore, they find applications in various fields such as separation technology, catalysis biomedical science, and nanocomposite material engineering.

First of all 4, in the context of this work, we present 4 samples of (Zn, Al) LDHs, representative of the 2 hosted anions (Cl^- and NO_3^-), prepared with a simple single-phase hydrothermal technique, using Zn salt as a precursor, deposited on sheets of Al, active as reagent and as a substrate. These preliminary samples, grown for 6 and 24 hours, were intercalated with spermidine and putrescine. Later, (Zn, Al) LDH powders obtained by coprecipitation and intercalated with amino acid cysteine were studied. The properties of LDH nanoplatelets were analysed by surface-sensitive techniques. X-ray photoelectron spectroscopy, energy dispersive X-ray spectroscopy, and possibly ultraviolet photoelectron spectroscopy (spectroscopy techniques) have been exploited to investigate the composition of the samples. The structure of LDHs was inspected by X-ray diffraction, whereas the morphology was investigated by scanning electron microscopy.

KEYWORDS

cysteine intercalation, layered double hydroxides, LDH, SEM, XPS, XRD

1 | INTRODUCTION

Layered double hydroxides (LDHs) are ionic lamellar compounds made up of positively charged brucite-like layers (cf Figure 1A). Anions and solvation molecules are contained within the interlayers regions for charge compensation. The metal cations occupy the centres of edge-sharing octahedra, whose vertexes contain hydroxide ions connected to form 2D sheets. The most widely studied LDHs accommodate both

divalent and trivalent metal cations. A generic formula¹⁻⁵ for these LDHs may be written as $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2] [\text{A}^{n-}_{x/n} \cdot m\text{H}_2\text{O}]$, where M^{2+} and M^{3+} are divalent and trivalent metal cations in octahedral holes, respectively. M^{3+} cations partially substitute M^{2+} , making the hydroxide sheets positively charged and requiring intercalation of n -valent anions A^{n-} . The $\text{M}^{2+}/(\text{M}^{2+} + \text{M}^{3+})$ ratio x is usually in the range $0.1 \leq x \leq 0.5$.

The possibility of synthesizing low-dimensional solids is of great importance in many fields of research and applications. Two-

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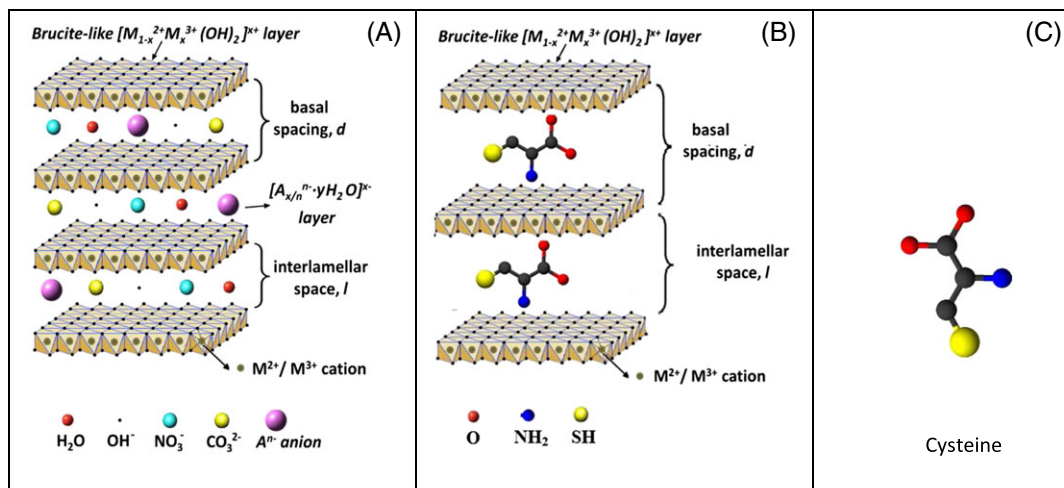


FIGURE 1 General structure of layered double hydroxide compounds intercalated by (A) anionic species and (B) cysteine; (C) cysteine basic structure

dimensional nanosheets, some nanometres thick and few microns (submicrons) wide, represent ideal 2D quantum systems for studies in fundamental physics and as building structure for functionalized solids.⁶ The incorporation of biological molecules into LDHs has become of interest in recent years, and materials such as DNA,⁷ ATP,⁸ amino acids or enzymes,^{9,10} and vitamins¹¹ have been stabilized in the interlayer space of LDHs. Therefore, spectroscopic surface analyses of LDH are basic. It has been repeatedly noted that the functional properties of such nanomaterials are closely related to the intercalation mechanism and to the coordination of oxygen and metals.^{1,12-14} In this article, we present the results obtained by intercalating cysteine in the samples of (Zn, Al) LDH grown with coprecipitation technique.

1.1 | Sample preparation

We started by implanting amine and spermidine in an (Zn, Al) LDH by low-temperature hydrothermal synthesis with the following specifics: 10mM concentration of $Zn(NO_3)_2$, 10mM concentration of the amine ($C_6H_{12}N_4$) plus spermidine, Al foil as substrate and reactants. The syntheses were performed at 80°C and with different times (6 and 24 h). Scanning electron microscopy images and energy dispersive X-ray spectroscopy analysis for spermidine are reported in Figure 2 (top) and Figure 2 (bottom), respectively.

Scanning electron microscopy images demonstrate that LDHs are well formed and shaped, densely and uniformly arranged on the substrate. Nevertheless, morphology strongly changes with synthesis

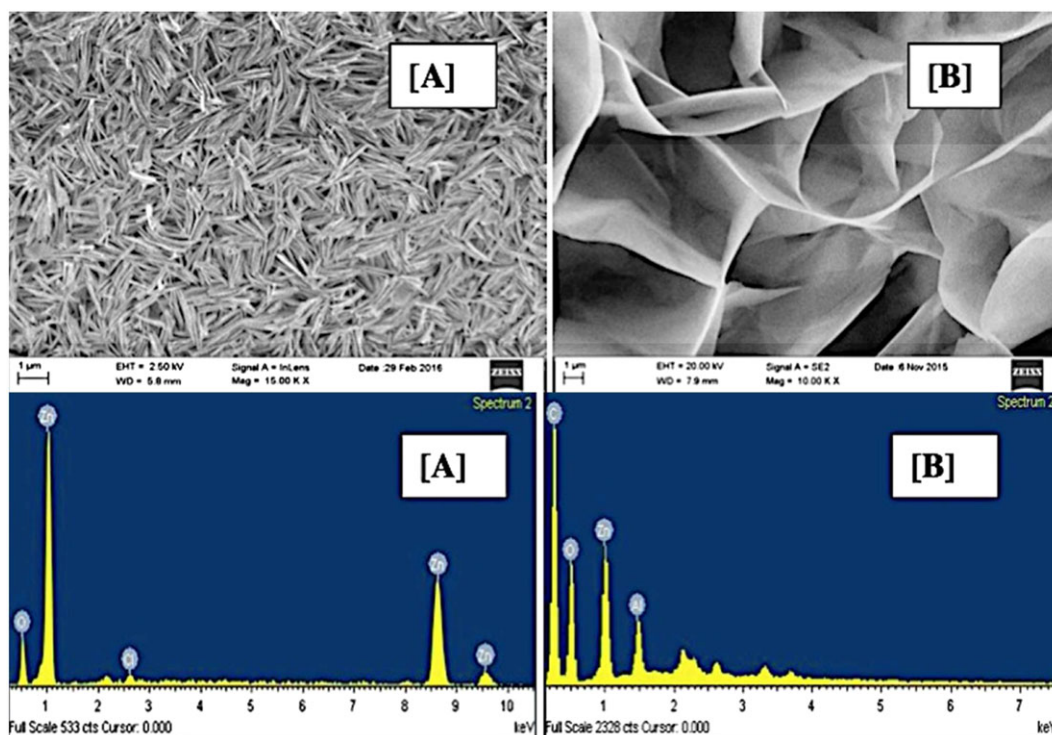


FIGURE 2 Scanning electron microscopy (top) and energy dispersive X-ray spectroscopy (bottom) images of spermidine-intercalated layered double hydroxide. Growth duration: A, 6 hours; B, 24 hours

duration: 24-hour samples show longer, thicker, and separated nanopetals. This is not negligible because various applications, including biomedical ones, are closely related to morphology of nanomaterials.

The energy dispersive X-ray spectroscopy analysis (performed by an energy dispersion X-ray analyser EDAX, INCA Energy 300, Oxford Inc, Abingdon, UK) showed the carbon content: low values for the 6-hour specimen, considerably higher ($\approx 67\%$) for the 24-hour growth specimen. This demonstrates that the amine has been intercalated into the layers. Analogous results were obtained for putrescine.

Motivated by those results, we tried the intercalation of another amine: cysteine. The growth technique adopted was that of coprecipitation, more effective for large biological molecules.

Coprecipitation method required preliminary studies to define the suitable aqueous solution for originating (Zn, Al) LDHs (the reference LDH) and the proper method to extract final products.

Experiments were conducted in a hot reactor. The slurry was then dried at high temperature at 180°C for 1 hour. Completed this preliminary phase, syntheses started including biological molecules into a solution containing sodium hydroxide, to guarantee a higher pH value (close to 11). Samples were prepared with the following specific:

Reference LDH: ZnCl_2 - 20mM, AlCl_3 10mM, NaOH to keep $\text{PH} \approx 11$, $\Delta t = 24$ hours, $T = 80^\circ\text{C}$;

Intercalated LDH (CY-LDH): ZnCl_2 - 20mM, AlCl_3 10mM, cysteine 20mM, NaOH to keep $\text{PH} \approx 11$, $\Delta t = 24$ hours, $T = 80^\circ\text{C}$.

1.2 | Analysis

The properties of reference LDH and cysteine-LDH (CY-LDH) samples were analysed by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

The XPS analysis on LDH planar substrates was conducted with an Escalab 250Xi (Thermo Fisher Scientific, UK) spectrometer provided with a monochromatic Al K α and ultraviolet He sources; electromagnetic lenses; electron and ion flood guns for charge neutralization; 6-channeltron detector. Intercalated powder samples were inspected by an Escalab MkII (VG Scientific, UK) equipped with an unmonochromatized source, electrostatic lens, and 5-channeltron detectors, to avoid charging problems and obtain results averaged over large sample area.

For pristine LDH samples, we considered an area of 1 mm in diameter at constant pass energy of 40 eV, large spot charge

compensation, and standard lens mode. For CY-LDH samples, the area had a diameter of 10 mm and pass energy of 20 eV. All the spectra were stable during the acquisition, ie, no sample modifications due to degassing of water or hydroxyl groups were observed.

Advantage v.5 software (Thermo Fisher Scientific, UK) was used for data processing. Shirley background subtraction and standard set of Scofield sensitivity factors were used for XPS quantification.

2 | RESULTS AND DISCUSSION

X-ray diffraction has been preliminarily applied to study all the samples (see Figure 3). Spectra recorded with Co-K α radiation confirm the hexagonal (Zn, Al) LDH crystal structure. Two basal reflections, {006} and {009}, give evidence of parallel-oriented LDH nanoplatelets giving a "c" value of about $22.29 \pm 0.01 \text{ \AA}$, in very good agreement with the literature. From nonbasal reflections (h or k $\neq 0$), the mean value for the "a" parameter was determined ($a = 3.06 \pm 0.01 \text{ \AA}$). To determine the lattice parameters, high-precision XRD peaks were collected with 2θ step of 0.005° and 10 seconds of counting time per step.

For CY-LDH sample, the 009 reflection is shifted towards lower angles, and this implies a higher $c = 28.98 \pm 0.01 \text{ \AA}$.^{1,2,15,16} The spacing between lamellas is wider, confirming the presence of the intercalated molecules. No appreciable differences on the "a" lattice parameter were observed. Namely, the CY-LDH one is $3.05 \pm 0.01 \text{ \AA}$.

In Table 1, results of elemental identification and quantification from XPS spectra, relative to the LDH and CY-LDH samples, at 0° and 30° collection angles to the sample normal, are reported.

The binding energy values of Al 2p and Zn 2p peaks indicated the main oxidation states of Al^{3+} and Zn^{2+} .

For better identification of the Zn chemical state, the modified Auger parameter α' was calculated, that is, $\alpha' = 1021.8(\text{BE}) + 987.4(\text{KE}) = 2009.2 \text{ eV}$, corresponding to the Zn^{2+} oxidation state.^{15,16}

The XPS analysis was applied to study the intercalation process and possible interaction mechanism of cysteine with LDH. As shown in Table 1, typical peaks of Zn 2p, Al 2p, O 1s, and C 1s were registered on the sample surface. Compared with pristine LDH, the cysteine insertion in the LDH interlayer caused a drastic decrement of Zn and disappearance of Al 2p, indicating the surface coverage with organic compound. In the peak fitting of C 1s spectrum of the reference LDH, 3 components were identified at BE of about 285, 288, and 290 eV.

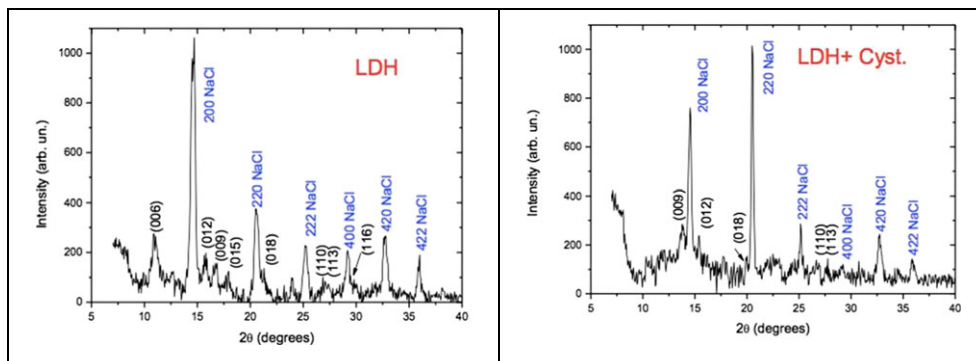


FIGURE 3 X-ray diffraction analysis of layered double hydroxide (LDH) and cysteine-LDH samples

TABLE 1 XPS quantitative results for LDH and CY-LDH samples

Peak	BE, eV	FWHM, eV	Atomic, %		Chemical State	Auger Parameter α' , eV
			0° Angle	30° Angle		
Reference LDH						
Al 2p _{3/2}	73.7	1.6	8.0	7.0	Al(OH) ₃	
C 1s A	285.0	2.3	13.4	23.3	Aliphatic	
C 1s B	287.9	2.3	2.1	1.5	Carboxyl O—C=O	
C 1s C	290.0	2.3	2.3	2.4	Carbonate	
Cl 2p	199.2	3.3	7.9	10.0	Chloride	
Na 1s	1072.5	2.1	2.5	3.6	Na(+1)	
O 1s A	530.3	2.2	12.4	7.7	Oxides	
O 1s B	531.8	2.2	34.8	31.4	OH ⁻	
Zn 2p _{3/2}	1021.8	2.3	16.6	13.0	Zn(+2)	2009.2
CY-LDH						
C 1s A	285.0	2.6	16.5	23.3	Aliphatic	
C 1s B	288.9	2.6	13.5	13.0	Carboxyl O—C=O	
Cl 2p	200.2	3.4	3.3	3.4	Chloride	
F 1s	689.2	0.7	0.7	1.0	Fluoride	
N 1s	399.3	2.5	2.9	2.3	NH ₂	
Na 1s A	1071.5	2.3	25.7	22.2	Na(+1) as in NaCl	
Na 1s B	1073.5	2.3	2.0	2.5	Na ₂ O	
O 1s	531.3	2.3	33.6	30.9	Oxides; OH ⁻	
S 2p	161.5	2.9	1.5	1.4	Sulphide	
Zn 2p _{3/2}	1021.5	1.0	0.3	0.2	Zn(+2)	2009.3

Abbreviations: BE, binding energy; FWHM, Full-Width Half Maximum; LDH, layered double hydroxide; CY-LDH, cysteine-layered double hydroxide; XPS, X-ray photoelectron spectroscopy.

The first one is attributed to the aliphatic ring carbon, whereas the other two are attributed to carboxylic and carbonate bonds, respectively. A considerable increase of C 1s intensity, in particular of carboxylic species, was observed after intercalation with cysteine. Even higher increase of Na amount was observed after this intercalation.

In the XPS measurements with increased surface sensitivity (30° angle), a noticeable increase of aliphatic carbon and chlorides was observed in the reference sample, indicating the surface contamination with these elements. Only a slight increase of aliphatic carbon was detected on the surface of both intercalated samples.

3 | CONCLUSIONS

In conclusion, we can trust that cysteine was intercalated in the interlamellar space of LDHs. The successful intercalation was confirmed by structural modifications, ie, increase of the “c” lattice parameter monitored by XRD, and surface analysis performed with XPS, which verified the inclusion of amino acid-related species. We think these results are quite promising. For these reasons, we intent to analyse better the chemical and structural properties of our intercalated LDH samples obtained in different growth conditions and with different types of intercalated substances. In particular, we would like to investigate the intercalation of another amino acid such as S-allil-mercaptocysteine,¹⁷ which is obtained from allyl-sulphate and garlic derivatives. It is considered one the best phytotherapeutic ingredients against melanoma. We could then check the possibility of applying LDHs for drug delivery. The need of a deep knowledge of the intercalated LDHs

structures and properties appears to be mandatory, also in connection with its possible toxicity.

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