



Morphology of Zn/Al layered double hydroxide nanosheets grown onto aluminum thin films



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ABSTRACT

Layered double hydroxide (LDH) nanosheets have been fabricated by a one-step, room-temperature, hydrothermal process on sputtered-aluminum thin substrates, in which the metal substrate acts as both reactant and support. The morphology, dimensions and composition of the obtained nanostructures have been characterized as a function of the substrate thickness by scanning electron microscopy (SEM), X-ray diffraction (XRD), energy dispersion spectroscopy (EDS) and photoluminescence measurements. While the lateral size of the observed LDH nanosheets depends on the available aluminum, the stoichiometry does not change appreciably. Even for the lowest values of the aluminum thickness, the excess zinc does not alter the chemical composition of LDH, but rather produces ZnO nanorods that show the characteristic defect-related broad visible photoluminescence centered at approximately 600 nm. The results show that a controlled growth of Zn/Al LDH nanosheets can be achieved onto sputtered aluminum thin layers with thicknesses as low as 10 nm, which can be important for the integration of LDH on generic substrates.

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1. Introduction

The ability to produce advanced low-dimensional building blocks, such as nanoparticles, nanorods and nanosheets to be assembled and integrated into functional three-dimensional networks are crucial challenges for the development of innovative devices [1]. Layered double hydroxides (LDHs) are ionic lamellar materials belonging to the group of anionic clays, whose general structure is based on brucite-like layers (Fig. 1), containing a divalent M^{2+} cation coordinated with six OH^- hydroxyl groups [2–5]. The substitution of the M^{2+} metal (for instance Ca^{2+} , Zn^{2+} , Mg^{2+} , Ni^{2+}), with a trivalent M^{3+} cation gives rise to the infinite repetition of positively-charged sheets (lamellas) alternating with charge-counterbalancing A^{n-} ions. Interestingly, this hydrotalcite-like layered structure can host even complex organic molecules, such as drugs and biomolecules, intercalated in the large interlamellar space.

This surprisingly large flexibility in composition and functionalization allows a large variety of applications based on *ad hoc* engineered LDHs [5,6]. For instance, superhydrophobic surfaces can be fabricated (in particular with Ni/Al LDHs) by combining an appropriate surface roughness with low-energy surface [7,8]. Moreover, due to the capacity to exchange ions and to host anions in interlamellar template, LDHs have been investigated as additives in organic anti-corrosion coatings [9,10], in flame retardants [11], in clay-modified electrodes for electroanalytical applications [12] and biosensors for water treatment and purification [13–15]. LDHs have also aroused great interest for biomedical applications. Due to the easy preparation, low toxicity, good biocompatibility, and robust protection of the intercalated molecules, LDHs have been studied as efficient systems for drugs and genes reservoir and delivery [16–18]. Finally, LDHs have recently been suggested as promising nanocontainers for UV-absorber molecules [19], to preserve biodegradable polymers from photodegradation and aging, and for controlled release of corrosion inhibitor agents, to prevent corrosion processes in metallic surfaces [20].

Good-quality LDHs can be synthesized by different techniques usually based on co-precipitation method [21]. Aluminum-containing materials, i.e. alumina powders, have also been used

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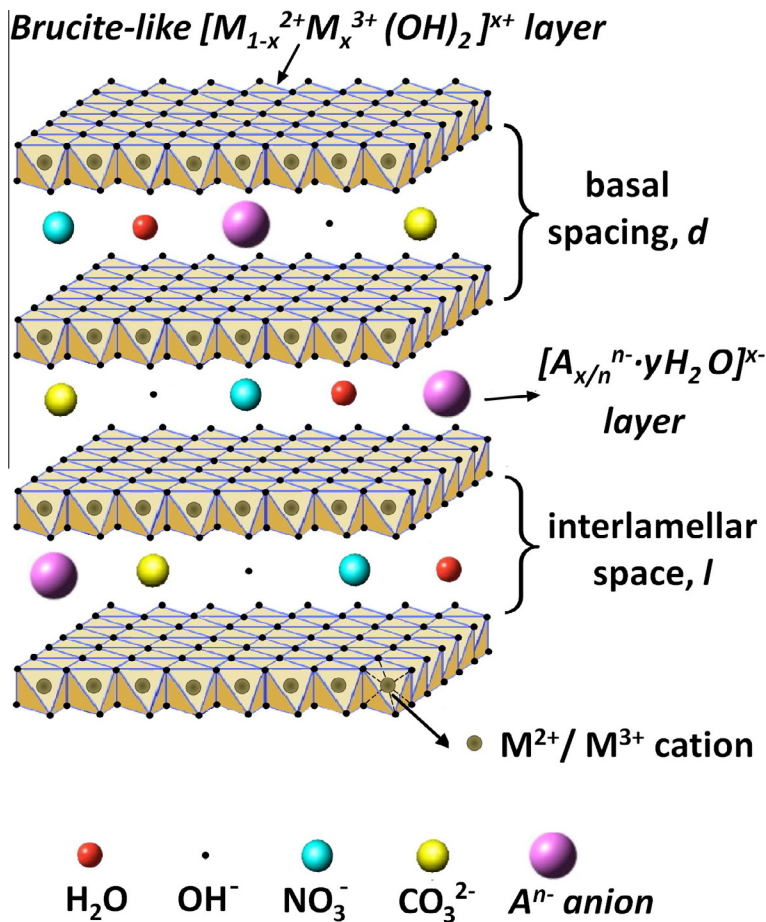


Fig. 1. General crystal structure of LDH compounds. Some possible anionic hosts in the interlamellar space are indicated.

to produce LDH nanoscale precipitates [22–24] that can eventually be collected and deposited on specific substrates. This strategy, however, presents the severe drawback of poor adhesion of the precipitated nanostructures, a detrimental disadvantage in many applications. More recently, two groups [25–27] demonstrated the possibility of growing very stable films of LDH nanocrystallites, in particular Zn/Al LDHs, by a simple one-step, room-temperature technique, by immersing aluminum thick foils in a solution containing zinc nitrate or acetate. Unlike the usual hydrothermal growth, only a single salt is used to provide the divalent metal Zn^{2+} , while the trivalent one (Al^{3+}) is provided by the foil that also acts as support, in this way greatly improving the adhesion. This route could easily allow growing Zn/Al LDHs (and in principle other Me^{2+}/Me^{3+} , LDHs) onto any kind of surface, other than aluminum thick foils, provided that an aluminum thin film is previously deposited. By using this technique, LDHs nanostructures have been realized on rigid transparent materials [28] and could be fabricated even on flexible substrates such as plastic films, given the low temperature and the almost neutral pH of the used chemical solutions.

In this paper we have investigated the influence of the aluminum thin-film thickness on the hydrothermal growth of Zn/Al LDHs, by lowering the thickness from 100 nm to as low as 5 nm. The nanostructure morphology, the lateral thickness of LDH nanosheets and their composition have been characterized by Scanning Electron Microscopy (SEM), X-ray diffraction (XRD), Energy Dispersive Spectroscopy (EDS) and photoluminescence measurements and correlated to the thickness of the pre-deposited aluminum layer.

2. Experimental section

2.1. Sample preparation

Silicon wafers (111) oriented were purchased by Siltronic and coated with an aluminum layer by means of Magnetron sputtering DC. Five different values of the aluminum-coating thickness were chosen for the successive hydrothermal growth: 100, 50, 25, 10 and 5 nm.

The hydrothermal growth onto the aluminum-coated wafers was carried out by using a nutrient solution composed of a 1:1 ratio of zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and hexamethylenetetramine ($C_6H_{12}N_4$) at 5 mM concentration. Hexamethylenetetramine was used as a pH regulator, through the hydrolyzation and release of ammonia at high temperature [29]. During the growth, the samples, anchored to a 45° tilted Teflon substrate, were kept in the middle of the solution bottle by means of Teflon screws. The growth temperature and time were fixed at 75 °C and 24 h, respectively.

After the growth, the sample was cooled down at room temperature and then washed with acetone or ethanol to remove the residuals on top of the LDH surface. Further details on growth and dependence of nanoplatelets morphology on the aluminum thickness and growth temperature will be given elsewhere [30].

2.2. Characterization techniques

Steady-state room-temperature photoluminescence (PL) spectra were recorded on a standard laboratory set-up with a

photomultiplier optical detector (Hamamatsu R3896) located at the output port of 25-cm monochromator (Oriel Cornerstone 260-74100). The excitation light beam was provided by the monochromatized output of a Hg (Xe) 200-W discharge lamp (Oriel 66485) at the wavelength $\lambda_{\text{ex}} = 290$ nm. Both the excitation and emission spectra were fully corrected by using the set-up calibration curve obtained with a reference black-body lamp and standard anthracene solutions. A spectral band-pass of 2 nm was used for both the excitation and emission monochromators.

The surface morphology and the elemental composition of the samples (EDS) was observed by a field emission scanning electron microscope (FESEM), model LEO SUPRA 1250 Oberkochen, Germany, and energy dispersion X-ray analysis (EDAX, INCA Energy 300, Oxford Inc., Abingdon, UK), respectively. Structural properties of films were determined by X-ray diffraction experiments, performed with a RIGAKU-Geigerflex θ - 2θ Bragg-Brentano diffractometer equipped with a Cu target ($\lambda_{\text{Cu K}\alpha} = 1.54186$ Å).

3. Results and discussion

3.1. SEM and XRD studies

Figs. 2–5 show the SEM micrographs of samples growth onto aluminum layers with different thicknesses. The morphology of the observed nanostructures shows a cauliflower-like shape, very similar to that reported by other groups [25,31] in LDHs grown by using comparable wet-chemistry methods on thick aluminum foils. The presence of LDH in the present experiment is confirmed by the XRD pattern of the sample with a 100-nm-aluminum thickness, shown in Fig. 6. The typical XRD reflections of LDH structure [19,33] are observed and indexed in the figure, along with some other unassigned reflections that could belong to Zn or Al phases.

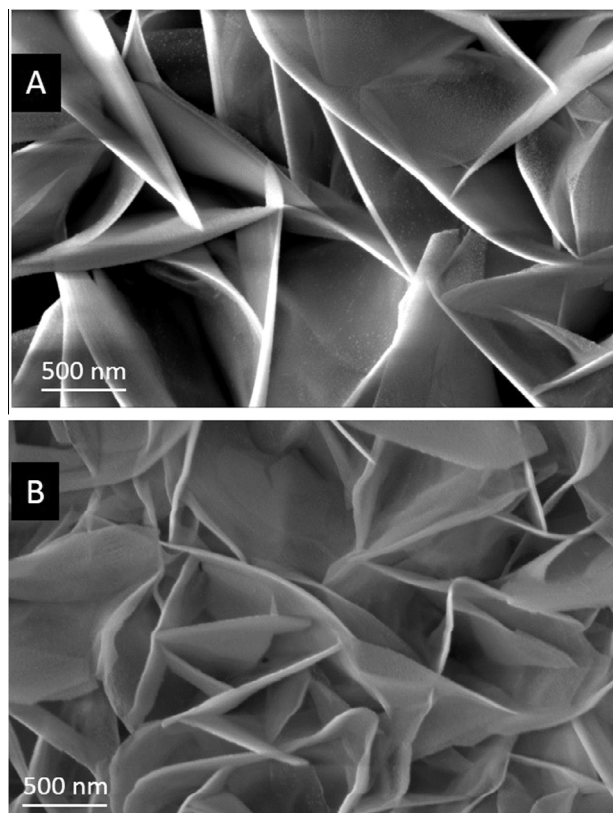


Fig. 2. High-magnification SEM images of Zn–Al LDHs grown onto Al thin layers by employing different layer thicknesses: (A) 100 nm and (B) 50 nm.

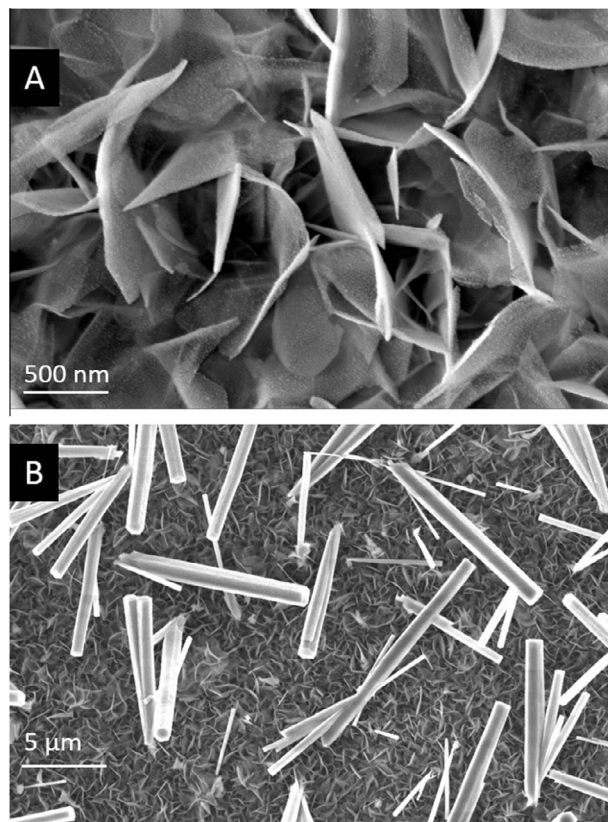


Fig. 3. SEM images of Zn–Al LDHs grown onto an Al layer with a thickness of 25 nm: (A) High magnification and (B) low magnification.

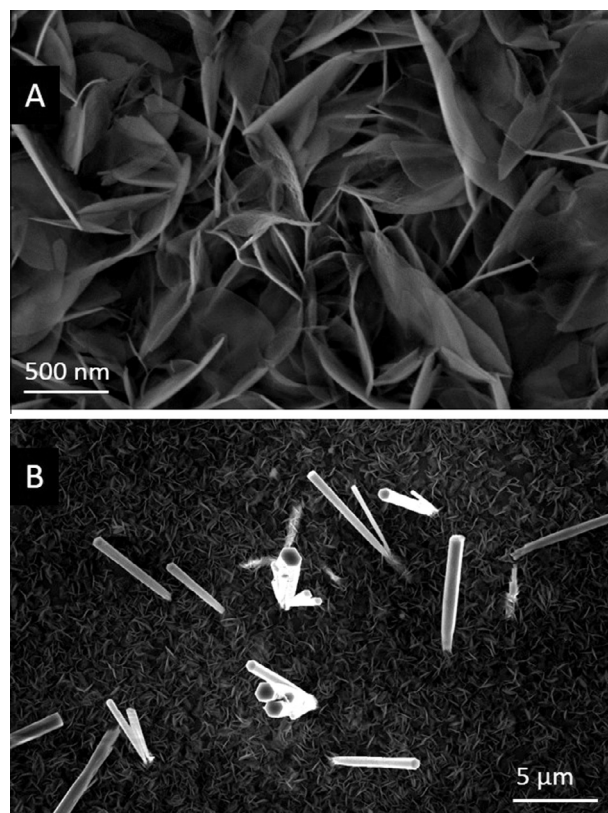


Fig. 4. SEM images of Zn–Al LDHs grown onto an Al layer with a thickness of 10 nm: (A) High magnification and (B) low magnification.

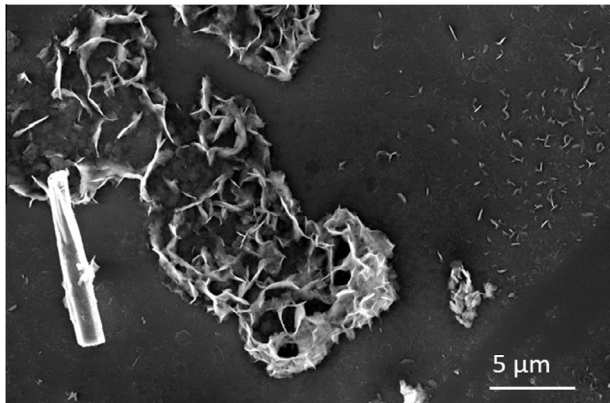


Fig. 5. SEM image of Zn–Al LDHs grown onto an Al layer with a thickness of 5 nm.

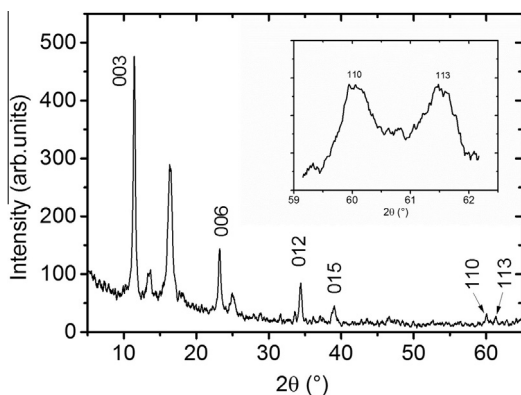


Fig. 6. XRD pattern of Zn–Al LDH grown onto a 100-nm-thick aluminum layer. The most representative reflections of LDH phase are indexed. Inset shows the XRD patterns in the range of the (110) and (113) reflections.

By applying the conventional formulas for the hexagonal structure to the (110) peak position, we could calculate the value of the lattice constant $a = 0.3081$ nm. Using the available data on a in the literature about Zn–Al LDHs [32,33], the zinc to aluminum content ratio was estimated to be close to 4:1. This value, even though appreciably lower than that derived from EDS measurements (not reported here) $Zn/Al = 6$, indicates a growth of LDH in excess of Zn.

The use of an aluminum thin film, however, enables to observe some significant differences as the film thickness is varied. Specifically, the samples with an aluminum thickness of 100 and 50 nm (Fig. 2A and B respectively) show the presence of well-formed curved nanosheets with a lateral dimension of approximately 40 and 30 nm, respectively. When the aluminum thickness is decreased to 25 nm (Fig. 3A) and down to 10 nm (Fig. 4A), the nanostructures become appreciably smaller (average lateral thickness of 15 and 10 nm, respectively), with a greater number density and a less regular shape. More significantly, sparse hexagonal nanorods, presumably ZnO nanorods, appear on the surface of the sample as shown by the lower-magnification larger-field SEM images of the same samples (Figs. 3B and 4B, respectively).

Interestingly, even though ZnO nanorods always form in the nutrient solution, there is no presence of ZnO nanorods on LDH at the higher values of the aluminum thickness (100 nm and 50 nm). In other words, ZnO nanorods form on the LDH only when the aluminum thickness goes down to 25 nm and to lower values. This effect could be explained by the fact that the aluminum coating in these samples is so thin that it is insufficient to completely

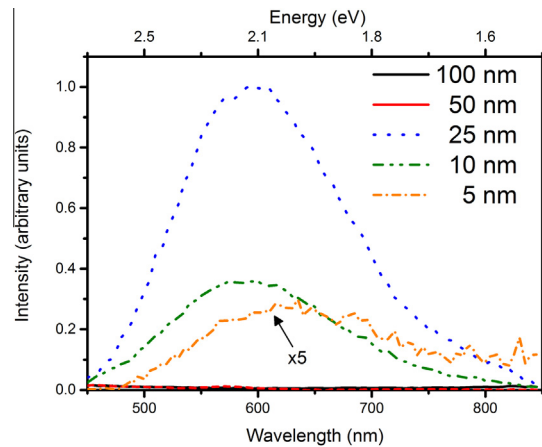


Fig. 7. Room temperature PL spectra of LDH samples grown onto aluminum layers of different thicknesses.

consume the locally present Zn^{2+} zinc ions. This changes the growth equilibrium and the excess zinc does not enter the LDH structure but rather produces ZnO nanorods that partially deposit onto the sample while mostly form a white precipitate at the bottom of the bottle. When the aluminum thickness is further decreased to 5 nm (Fig. 5), the available aluminum content is so low that only nano-islands of partially-formed LDH structures with ill-defined shape are formed and only few nanorods can be observed.

3.2. PL analysis

The presence of ZnO nanorods in some of the samples also reflects in the respective PL spectra reported in Fig. 7. All of the spectra are excited at $\lambda_{exc} = 290$ nm, that is the typical wavelength for exciting both the bulk and the defect-related electronic transitions of ZnO [34,35], and reported according to their actual relative intensity. By comparison with the SEM images, it is evident that a broad visible emission, centered at 600 nm, is observed only in those samples where nanorods appear (i.e. with aluminum thickness of 5, 10 and 25 nm). In addition, the intensity of the PL signal clearly increases with increasing number density of nanorods as observed with SEM. Conversely, in samples where nanorods cannot be found, no PL signal can be appreciated out of the noise, as it is normally expected in pure LDH. Furthermore, in those few samples where slight macroscopic inhomogeneities were found across the surface, the PL intensity correlated to the nanorods number density over the different areas of the sample, thus confirming that PL originates from the ZnO nanorods. Broad emission bands in the range 500–650 nm are typical of deep-level emission (DLE) from intrinsic-defect and/or impurity states in ZnO nanorods, whether pure [36,37] or doped with different transition metals [38–39] or, more appropriately in the present case, with aluminum [42]. In our samples, the presence of a DLE band confirms that the progressive decrease of the available aluminum, with decreasing substrate thickness, gives rise to the growth of Al-doped ZnO nanorods as competitive nanostructures with respect to LDH nanosheets. From this point of view, the slight red-shift of the PL band observed in the sample with the thinnest aluminum coating (5 nm) can be explained by the dependence of the DLE transition-energy on the dopant-aluminum content [39–41].

4. Conclusions

In this paper we have grown Zn/Al LDH nanostructures by a simple one-step hydrothermal method onto aluminum thin layers

that act as both reactant and support. The results show that the typical well-formed curved LDH nanoplatelets grow uniformly onto the substrate surface even for values of the aluminum-layer thickness as low as 10 nm. For a thickness equal to or less than 25 nm, however, sparse ZnO nanorods also appear onto the LDH surface, as also revealed by the typical defect-related visible photoluminescence under UV excitation. Presumably, such associated ZnO nanostructures form as a result of the low content of the available aluminum and consequent excess zinc. Interestingly, this effect seems to prevent LDH from changing its morphology and composition, even though the lateral thickness of LDH nanoplatelets decreases appreciably with the aluminum thickness while the nanoplatelets become smaller and with a greater number density. Our results confirm that the thin-film deposition of aluminum, even with thicknesses as low as 10 nm, can represent an extremely simple and cost-effective strategy for the growth of LDH on practically any substrate, including flexible substrates.

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