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Organo-layered double hydroxides composite thin films deposited by laser techniques

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ABSTRACT

We used laser techniques to create hydrophobic thin films of layered double hydroxides (LDHs) and organo-modified LDHs. A LDH based on Zn-Al with Zn^{2+}/Al^{3+} ratio of 2.5 was used as host material, while dodecyl sulfate (DS), which is an organic surfactant, acted as guest material. Pulsed laser deposition (PLD) and matrix assisted pulsed laser evaporation (MAPLE) were employed for the growth of the films. The organic anions were intercalated in co-precipitation step. The powders were subsequently used either as materials for MAPLE, or they were pressed and used as targets for PLD. The surface topography of the thin films was investigated by atomic force microscopy (AFM), the crystallographic structure of the powders and films was checked by X-ray diffraction. FTIR spectroscopy was used to evidence DS interlayer intercalation, both for powders and the derived films. Contact angle measurements were performed in order to establish the wettability properties of the as-prepared thin films, in view of functionalization applications as hydrophobic surfaces, owing to the effect of DS intercalation.

1. Introduction

Layered double hydroxides (LDHs) are a large class of inorganic materials, having as general formula, $[M^{2+}_{1-x}M^{3+}_{x}(OH_2)]^{x+}[A^{n-}]_{x/n}$ mH_2O where M^{2+} and M^{3+} are divalent and trivalent cations that occupy octahedral positions in the hydroxide layers, A^{n-} is an interlayer anion and x is the molar ratio [1]. The flexibility of their chemical composition allows the preparation of LDHs having a wide variety of properties, making them promising materials for applications in different fields such as catalysis, pollutants absorption, additives or precursors [2–5].

The anionic exchange capacity of LDHs is utilized to incorporate surfactant organic anions into the interlayer space in order to obtain organo-LDHs [1,6–8]. The ability to transform the LDH hydrophilic surface to hydrophobic and to access the interlayer region can extend the applicability of LDHs toward different types of functional nanocomposites [9–13]. The capacity of this new emerging class of multifunctional LDH based composite to preserve or to develop new properties as thin films is an open topic. Research on LDH films is expanding, in view of their applications as sensors [14,15], electrodes [16], corrosion-resistant coatings [11,12,17] etc. Usually, the LDH films are prepared by two methods: physical deposition and in situ growth, i.e. substrate-induced growth. We have previously reported on the ability of pulsed laser deposition (PLD) and matrix assisted pulsed laser evaporation (MAPLE) [18–20] to produce adherent, well oriented LDH films. In particular, hybrid LDH/polymer structures were transferred onto silicon substrates using MAPLE [20]. The targets used in the above study are organo-LDH composites accommodating the organic guest molecule in the interlayer space. In this study we used targets of pristine ZnAl based LDHs (Zn/Al molar ratio of 2.5) and intercalated dodecyl sulfate-LDHs (DS-ZnAl-LDHs) to obtain composite films. We performed a comparative study of the performance of two laser techniques in producing films which preserve the complex structures of the targets and we discuss the derived wettability properties.

2. Materials and characterization methods

2.1. Powders

All the chemicals used for the preparation of the ZnAl-LDHs and organo-modified LDHs were of analytical grade or of the highest purity commercially available.

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The pristine ZnAl-LDH powder was prepared via coprecipitation at 40 °C under low supersaturation conditions, pH 9.5–10. $Zn(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ anhydrous Na_2CO_3 and NaOH were the raw materials. The same coprecipitation method described by Reichle [21] and Carriazo et al. [22] was used. The molar ratio of Zn/Al was 2.5. The steps followed to obtain the final LDH powder were similar to those used for the preparation of MgAl-LDHs [23]. In the following we will refer to this powder as Zn2.5Al. The organo-modified LDHs were prepared using two methods: direct coprecipitation and, reconstruction via the “memory effect”. The coprecipitation method used an adapted protocol reported by Du et al. [24]. The raw materials were $Zn(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ (Zn/Al molar ratio of 2.5), and sodium dodecyl sulfate (SDS = $NaC_{12}H_{25}SO_4$, SDS/Al molar ratio of 1.5). Sodium hydroxide was used for pH adjustment (pH = 9.5–10). The final powder, labeled PZn2.5Al-DS, was obtained following the same procedure as for the Zn2.5Al powder. The DS intercalation via reconstruction occurred by immersing the mixed oxide powder derived from the gentle calcination (18 h at 460 °C in air flow) of the Zn2.5Al powder in an aqueous solution of SDS (SDS/Al molar ratio of 1.5). The immersion occurred at room temperature for 24 h. The recovered solid powder was labeled RZn2.5Al-DS.

X-ray diffraction – XRD (PANalytical X’Pert MPD system, λCuKα = 1.5418 Å) and Fourier transform infrared spectroscopy – FTIR (JASCO FTIR 6300 spectrometer equipped with ATR Specac Golden Gate unit) were the characterization techniques used to evidence the crystallographic structure and the intercalation of the dodecyl sulfate anions, respectively. The water contact angles were measured on the dry pressed pellets prepared as targets for PLD depositions. Contact angle (CA) measurements were performed at room temperature using a Contact Angle Tensiometer CAM 200 from KSV Instruments.

2.2. Thin films

The targets to be used in PLD experiments were dry pressed pellets obtained from the prepared Zn2.5Al, PZn2.5Al-DS and RZn2.5Al-DS powders. A Nd:YAG laser working at 1064 nm and having a 10 Hz pulse repetition rate was used. The PLD films were deposited at room temperature on silicon substrates following 12,000 pulses at fluences between 1 and 3 J/cm^2.

MAPLE thin films of Zn2.5Al, PZn2.5Al-DS and RZn2.5Al-DS were obtained using the fourth harmonic of a Nd:YAG laser (266 nm) having a pulse width of 5 ns and working at a pulse repetition rate of 10 Hz. The laser fluence was 1–2 J/cm^2. The Zn2.5Al, PZn2.5Al-DS and RZn2.5Al-DS powders (10% w/w) were mixed in water and ethanol (1:1), then frozen and used as targets. The films were grown on silicon substrates placed at 4 cm in front of the target and parallel to it following ablation by 80,000 pulses.

The XRD patterns were collected in grazing incidence geometry (GI angle of 0.25°). The FTIR spectra were recorded in the 400–4000 cm^{-1} range, with a resolution of 4 cm^{-1} and averaging upon 1024 scans. The surface morphology of the films was examined by atomic force microscopy (AFM), using a Park XE-100 system with silicon nitride cantilevers in non-contact mode. The water contact angles were measured using a KSV CAM101 optical microscope, with water drops of 0.5–1 µL.

3. Results and discussion

3.1. Powders

The XRD patterns of the powders prepared to be used as targets are presented in Fig. 1. The pristine ZnAl-LDH (sample Zn2.5Al) exhibits the typical pattern of a carbonate-layered double hydroxide material (JCPDS card no. 048-1022) with an R3m rhombohedral symmetry and was Miller indexed in a hexagonal lattice. The XRD pattern of the PZ2.5Al-DS sample reveals a shift of all the basal reflections toward small angles, which, along with the appearance of higher order peaks, is indicative of dodecyl sulfate anion intercalation in the interlayer free space. The XRD pattern of the RZn2.5Al-DS sample displays a mixture between a dominant modified DS-LDH, with basal reflections shifted toward low angles, and a small amount of a carbonate LDH phase, thus marking a partial DS intercalation. The lattice parameters c, calculated as $c = 3/2(d_{003} + 2d_{006})$, and a, expressed as $a = 2d110$ are listed in Table 1. Given the 0.48 nm thickness of the brucite-type layer [25], the interlayer free space values included in Table 1 are slighter smaller than the reported value of 2.08 nm of the DS molecule length [26,27], which indicates a tilted arrangement of the DS anions inside the LDH gallery.

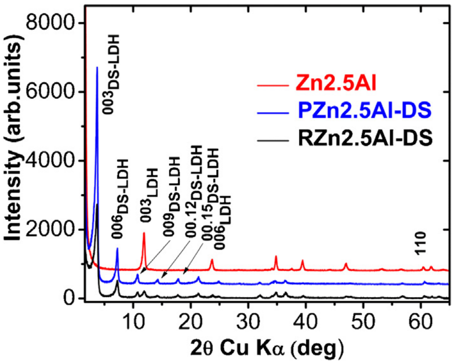

Fig. 1. The XRD pattern of the pristine Zn2.5 Al, PZ2.5Al-DS and of the RZn2.5Al-DS powders.

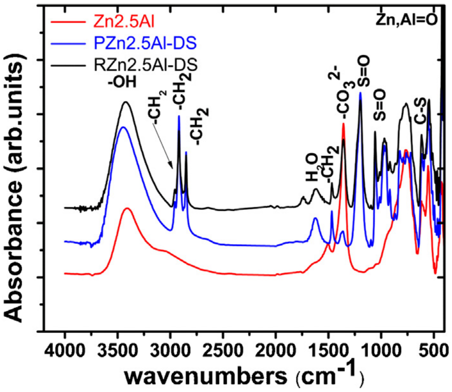

Fig. 2. The FTIR spectra of the Zn2.5 Al, PZ2.5Al-DS and RZn2.5Al-DS powders.

FTIR further confirms that the DS was successfully intercalated into the LDH, for both modified samples. In the pristine Zn2.5Al LDH structure, carbonate ion absorptions were revealed by the 1358 cm^{-1} asymmetric stretching mode ($\nu3$), 829 cm^{-1} for the out of plane bending mode ($\nu2$) and 693 cm^{-1} for the in plane bending mode (Fig. 2). The $\nu3$ and $\nu2$ bands are shifted to lower wavenumbers in comparison with IR vibrations positions of free $CO_3{}^{2-}$ anions in solution [26] due to a decrease in symmetry upon intercalation. After DS intercalation, the intensities of these absorption bands were reduced, in particular for the PZn2.5Al-DS powder. The result for the RZn2.5Al-DS sample is consistent with the presence of a small amount of unmodified LDH revealed by XRD measurement. The presence of the organic molecules in the modified LDH structures is further confirmed by the appearance of characteristic peaks at 2956, 2918 and 2850 cm^{-1} (ascribed to dodecyl sulfate counterions) corresponding to $-CH_2$ stretching vibrations, along with

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