

# Synthesis and characterization of Cd–Cr and Zn–Cd–Cr layered double hydroxides intercalated with dodecyl sulfate

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## Abstract

Cd–Cr and Zn–Cd–Cr layered double hydroxides (CdCr-LDH and ZnCdCr-LDH) containing alkyl sulfate as the interlamellar anion have been prepared through a coprecipitation technique. The resulting compounds were characterized using X-ray diffraction, infrared spectroscopy, thermogravimetric analysis, and scanning electron microscopy. Magnetic property measurements indicate that antiferromagnetic interactions occur between the chromium ions in the two compounds at low temperatures. The introduction of zinc influences the ligand field of Cr<sup>III</sup> and the Cr<sup>III</sup>–Cr<sup>III</sup> interactions in the LDH compound. It is found that both CdCr-LDH and ZnCdCr-LDH can be delaminated by dispersion in formamide, leading to translucent and stable colloidal solutions.

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**Keywords:** Layered double hydroxide; Chromium; Cadmium; Zinc; Magnetic properties

## 1. Introduction

Inorganic layered compounds are useful host materials between sheets of which guest species can be intercalated and novel composites with various functions can be obtained through intercalation [1–3]. Among the layered compounds, layered double hydroxides (LDHs) have received considerable attention due to their interesting properties and wide applications as catalysts, catalyst precursors or catalyst supports, adsorbents, anion exchangers, medicine stabilizers, ionic conductors and polymer stabilizers [4–15]. LDHs can be represented by the general formula  $[M_{1-x}^{II}M_x^{III}(\text{OH})_2]^{x+}A^{m-}_{x/m} \cdot n\text{H}_2\text{O}$ , where M<sup>II</sup> stands for a divalent cation, M<sup>III</sup> a trivalent cation and A<sup>m-</sup> an anion [16]. From the structure point of view, the metallic cations in an LDH material are located in octahedral  $[M(\text{OH})_6]$  units which share edges to form  $M(\text{OH})_2$  layers with the brucite ( $\text{Mg}(\text{OH})_2$ ) structure, and the

partial substitution of the divalent cations by trivalent ones results in positive charges in the inorganic layers which are balanced by anions sandwiched between the layers [17–19]. The compositions of LDHs are versatile and it is possible to modulate the properties of LDHs by changing the M<sup>II</sup> and M<sup>III</sup> cations, their molar ratio, and the nature of the compensating anions [20]. In addition, the synthesis of LDHs containing three or more cations in the layers and the introduction of various anions between the layers are also feasible. Although a variety of LDHs have been synthesized with divalent metals such as Mg, Mn, Fe, Co, Ni, Cu, Zn, and Ca and trivalent metals such as Al, Cr, Mn, Fe, Co, La, and Y [18–21], only a few systems containing Cd appeared in the literature. Miyata and Kumura described the preparation of LDH containing Cd as the divalent metal, but it seemed that the obtained material was a mixture of the desired product and CdCO<sub>3</sub> [22]. Later on, Bao synthesized  $[\text{Mg}_6\text{Al}_2(\text{OH})_{16}][\text{CO}_3] \cdot 4\text{H}_2\text{O}$  in which Mg<sup>II</sup> was partially substituted by Cd<sup>II</sup> ions in the hydrotalcite, but no product was prepared with Cd alone as the divalent metal [23] until 1997 when Vichi

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and Alves reported the well-crystallized LDHs with Cd as the divalent metal and Al as the trivalent metal and nitrate and carbonate as the counter anions [17].

In this paper, we present the preparation of a new LDH compound containing Cd as the divalent metal and Cr as the trivalent metal (CdCr-LDH) and a ternary (Zn, Cd, Cr) metal hydroxide with the LDH structure (ZnCdCr-LDH) through a coprecipitation technique. Dodecyl sulfate (DS) has been used as the anion to intercalate the layers of these two compounds, which exhibit high structural order and can be exfoliated into single layers in formamide solution, providing new precursors to be used in assembly chemistry. Antiferromagnetic interactions between the Cr<sup>III</sup> centers have been observed for the as-prepared CdCr-LDH and ZnCdCr-LDH.

## 2. Experimental

### 2.1. Preparation

All reagents for synthesis were commercially available and used as received without further purification. The method of preparation of the LDHs was based on that described previously [24]. For the synthesis of CdCr-LDH, a solution of 0.02 mol Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and 0.01 mol Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O with a Cd<sup>II</sup>/Cr<sup>III</sup> ratio of 2/1 in 15.8 mL H<sub>2</sub>O was mixed with a solution of DS surfactant (0.02 mol sodium DS in 85 mL H<sub>2</sub>O). To the resulting solution was added dropwise a solution of 2 mol L<sup>-1</sup> NaOH until a particular pH (8.0) was reached and the system was aged at room temperature for 2 h. Subsequently, a gray-blue suspension was formed and the solid product was separated by centrifugation from the suspension, washed with distilled water and dried under vacuum. For the synthesis of ZnCdCr-LDH, a mixture of 0.02 mol Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 0.01 mol Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and 0.01 mol Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O in 15.8 mL H<sub>2</sub>O was used as the cation solution, and the final pH was adjusted to 8.0 using a 2 mol L<sup>-1</sup> NaOH solution as well. The rest of the preparation procedure was the same as that for the CdCr-LDH material. The resulting product appeared light pink in color. Exfoliation of the layered double hydroxides (CdCr-LDH and ZnCdCr-LDH) was realized through dispersion of 0.15 g as-prepared LDH material in 50 mL formamide with stirring at room temperature. The exfoliation process was completed in about three days and a clear colloidal solution was obtained.

### 2.2. Characterization

The powder X-ray diffraction (XRD) patterns were recorded on a Siemens D5005 diffractometer with CuK $\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation. The FT-IR spectra of the

samples dispersed in KBr pellets were obtained within 4000–500 cm<sup>-1</sup> wavenumber region on a Nicolet Impact 410 FTIR spectrometer. The thermogravimetric (TG) analyses were conducted on a Netzsch STA 449C thermal analyzer under a flow of dry air at a heating rate of 20 K min<sup>-1</sup>. The C, H, N, S elemental analysis was performed on a Perkin-Elmer 2400 elemental analyzer, whereas the metal contents were determined by inductively coupled plasma (ICP) analysis on a Perkin-Elmer Optima 3300DV ICP spectrometer. The UV-vis powder diffuse reflectance spectra were measured on a Perkin-Elmer Lambda 20 spectrometer. The scanning electron microscope (SEM) images were taken on a JEOL JSM-6700F electron microscope and the temperature-dependent magnetic susceptibility data were collected on a Quantum Design MPMS-XL-5 SQUID magnetometer under an applied field of 1000 or 10,000 Oe over the temperature range 2–300 K. To confirm the exfoliation of LDHs in the colloidal solution, atomic force microscope (AFM) images were obtained at room temperature in the tapping mode using a Digital Instruments Nanoscope IIIa AFM. Prior to imaging, the colloidal solution was diluted and dropped onto a mica substrate and dried under vacuum.

## 3. Results

Fig. 1 shows the SEM images for the two as-prepared LDHs compounds. It is seen that both compounds appear as irregular plate-like particles characteristic of sheet structure, and the particle diameter varies from 0.3 to 2  $\mu\text{m}$  for CdCr-LDH and from 2 to 70  $\mu\text{m}$  for ZnCdCr-LDH.

The powder XRD patterns for the as-synthesized samples are displayed in Fig. 2. As can be seen, both materials exhibit high structural order, and the typical diffraction peaks correspond to intercalated LDHs with layer separations in good agreement with those reported previously [24]. The basal spacings calculated from the XRD patterns are presented in Table 1. CdCr-LDH has a basal spacing of 26.9  $\text{\AA}$  whereas ZnCdCr-LDH has one of 27.4  $\text{\AA}$ . The introduction of the DS surfactants in the interlayer space of LDH is evidenced by IR spectroscopy and elemental analysis. Fig. 3 shows the FT-IR spectra of the samples. Besides a broad absorption band at around 3500 cm<sup>-1</sup> due to the presence of hydroxyl groups of LDH, the existence of C–H stretching at 2919, 2844 cm<sup>-1</sup> and C–H bending at around 1469 cm<sup>-1</sup> confirms the presence of the DS molecules in the sample. As expected, the absorption bands of the sulfate ion at 1255, 1226, 1083, 998, and 593 cm<sup>-1</sup> are also observed in the two LDH compounds. Absorption bands of nitrate (1380 cm<sup>-1</sup>) and carbonate (1450 cm<sup>-1</sup>) ions are not observed for CdCr-LDH and

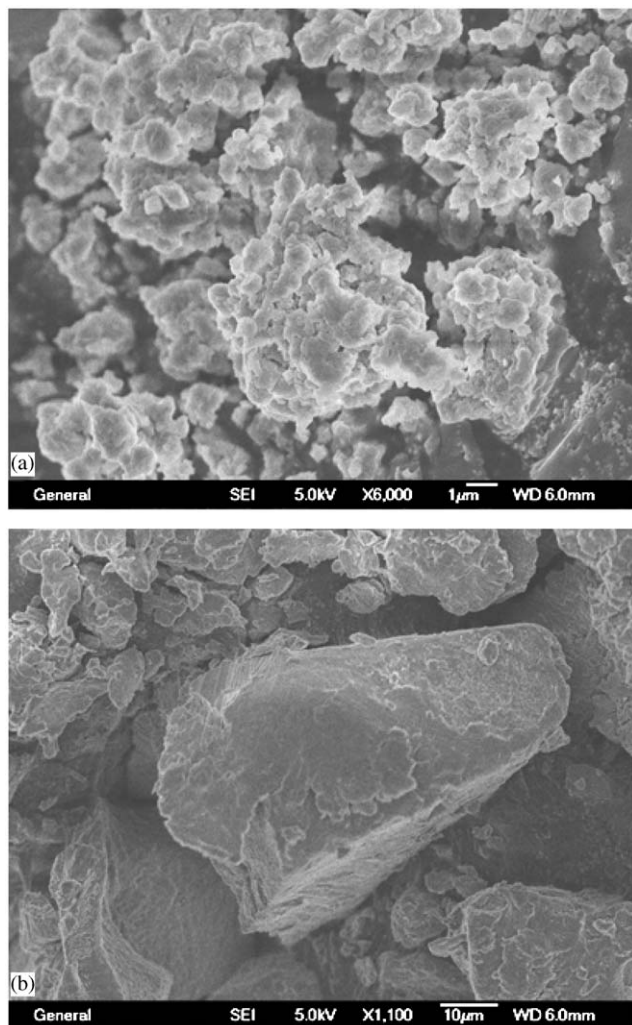


Fig. 1. The SEM images of (a) CdCr-LDH and (b) ZnCdCr-LDH.

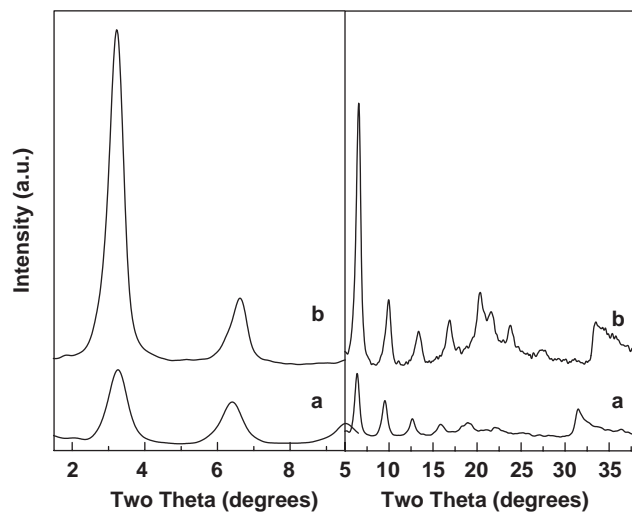


Fig. 2. Small (left) and wide (right) angle powder X-ray diffraction patterns for (a) CdCr-LDH and (b) ZnCdCr-LDH.

ZnCdCr-LDH, indicating that the compounds are highly pure in terms of intercalating anions.

The TG profiles of the two LDHs are presented in Fig. 4. For CdCr-LDH, the loss of surface water and interlayer water begins upon heating and is complete at about 180 °C, which is followed by the dehydroxylation in the temperature range 180–260 °C. The third main weight loss at 260–620 °C is attributable to the combustion of the DS. The TG curve of ZnCdCr-LDH shows two less-resolved weight losses over the whole temperature range. The first one in the temperature range 25–260 °C is due to the removal of adsorbed and interlayer water molecules whereas the second one at 260–700 °C corresponds to the concomitant dehydroxylation and the decomposition of the anionic surfactant chain from the interlayer region. The weight loss continues till 700 °C for ZnCdCr-LDH but it ends at around 620 °C for CdCr-LDH.

Fig. 5 shows the diffuse reflectance UV-vis spectra of the as-synthesized CdCr-LDH and ZnCdCr-LDH. There appear two distinct bands at 412 and 574 nm for CdCr-LDH and at 383 and 557 nm for ZnCdCr-LDH.

The temperature dependence data of the magnetic susceptibility were measured over the temperature range 2–300 K for CdCr-LDH and ZnCdCr-LDH. The results are shown as plots of  $\chi_M T$  and  $\chi_M^{-1}$  versus  $T$  for the two LDHs in Fig. 6. In Fig. 6a, the value of  $\chi_M T$  for CdCr-LDH appears to be  $0.41 \text{ cm}^3 \text{ K mol}^{-1}$  per formula unit at room temperature. As the temperature is lowered (from 300 to approximately 130 K), the  $\chi_M T$  shows a slight increase on cooling the temperature and reaches a maximum value of  $0.42 \text{ cm}^3 \text{ K mol}^{-1}$  at 130 K. Below this temperature, the  $\chi_M T$  value decreases smoothly to  $0.09 \text{ cm}^3 \text{ K mol}^{-1}$  at 2 K. For ZnCdCr-LDH (Fig. 6b), the observed value of  $\chi_M T$  is  $0.36 \text{ cm}^3 \text{ K mol}^{-1}$  per formula unit at room temperature, and it increases gradually with lowering the temperature and reaches a maximum of  $0.40 \text{ cm}^3 \text{ K mol}^{-1}$  at 90 K. Again, there is a continuous decrease in the value of  $\chi_M T$  for ZnCdCr-LDH as the temperature is lowered from 90 to 2 K, at which the value is  $0.07 \text{ cm}^3 \text{ K mol}^{-1}$ .

#### 4. Discussion

As is known, LDHs have been widely used in heterogeneous catalysis. The choice of different metal cations  $M^{\text{II}}$ ,  $M^{\text{III}}$  and their ratio make these materials suitable for modulation of catalytic properties. The combination of Cd and Cr to form new LDHs will extend the family of LDHs in terms of composition on one hand, and will vary the physical–chemical property of the LDH material on the other. In addition, upon calcination, the LDHs may transform to a homogeneous mixture of cadmium, chromium and/or zinc oxides with

Table 1  
Basal spacings and composition analysis data for CdCr-LDH and ZnCdCr-LDH

	Found (wt%)					Empirical formula	Basal spacing (Å)
	M <sup>IIa</sup>	M <sup>IIIa</sup>	S <sup>b</sup>	C <sup>b</sup>	H <sub>2</sub> O <sup>c</sup>		
CdCr-LDH	35.4(Cd)	7.21	4.32	19.9	5.2	Cd <sub>0.7</sub> Cr <sub>0.3</sub> (OH) <sub>2</sub> (C <sub>12</sub> H <sub>25</sub> SO <sub>4</sub> ) <sub>0.3</sub> ·0.7H <sub>2</sub> O	26.9
ZnCdCr-LDH	13.8(Cd) + 15.2(Zn)	6.26	3.70	17.8	14.6	Zn <sub>0.5</sub> Cd <sub>0.25</sub> Cr <sub>0.25</sub> (OH) <sub>2</sub> (C <sub>12</sub> H <sub>25</sub> SO <sub>4</sub> ) <sub>0.25</sub> ·1.7H <sub>2</sub> O	27.4

<sup>a</sup>From ICP.

<sup>b</sup>From elemental analysis.

<sup>c</sup>From TG.

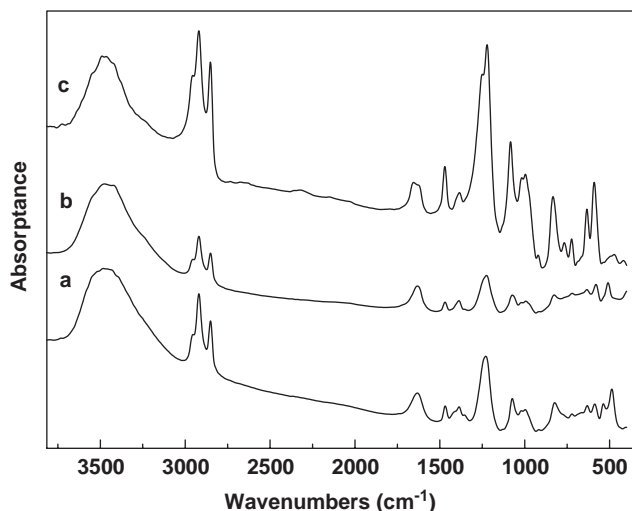


Fig. 3. IR spectra for (a) CdCr-LDH, (b) ZnCdCr-LDH and (c) C<sub>12</sub>H<sub>25</sub>SO<sub>4</sub>Na (DS, sodium dodecyl sulfate).

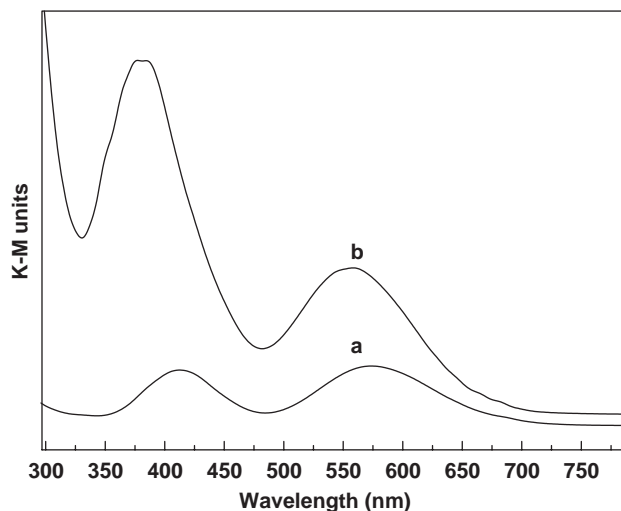


Fig. 5. The UV-vis diffuse reflectance spectra of the as-synthesized (a) CdCr-LDH and (b) ZnCdCr-LDH using BaSO<sub>4</sub> as the background.

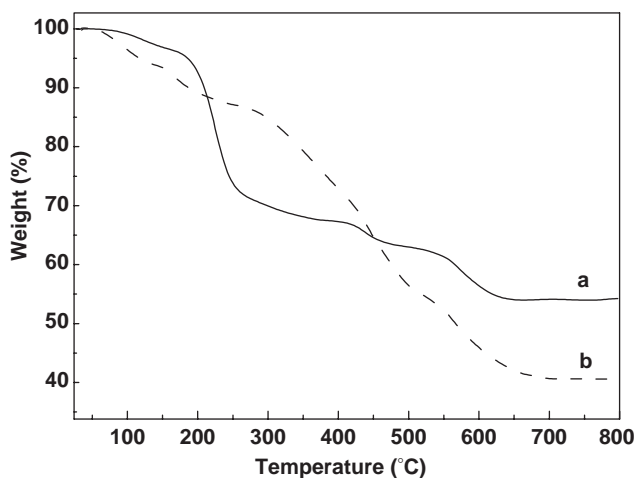


Fig. 4. TG curves of (a) CdCr-LDH and (b) ZnCdCr-LDH.

very small crystal sizes, which may find applications as multicomponent catalysts [13].

The incorporation of anions in LDHs can be realized through various methods, such as direct synthesis involving coprecipitation technique in the presence of

guest species [24], conventional anion exchange reaction [25], or heat treatment of LDHs containing carbonate as anion followed by mixing with an aqueous solution of guest molecules [26]. Among these methods, the coprecipitation one is most employed as it is simple and the impurity resulted from other anions is least. In our work, we also used the coprecipitation methods to prepare LDHs intercalated with DS at a constant pH. The synthesis of the LDHs at a constant pH is performed by addition of the solution of the cations to a solution of the intercalating anion, using a NaOH solution to retain the constant pH value. The ICP and CHNS elemental analyses in combination with the TG results give rise to compositions Cd<sub>0.7</sub>Cr<sub>0.3</sub>(OH)<sub>2</sub>(C<sub>12</sub>H<sub>25</sub>SO<sub>4</sub>)<sub>0.3</sub>·0.7H<sub>2</sub>O for CdCr-LDH and Zn<sub>0.5</sub>Cd<sub>0.25</sub>Cr<sub>0.25</sub>(OH)<sub>2</sub>(C<sub>12</sub>H<sub>25</sub>SO<sub>4</sub>)<sub>0.25</sub>·1.7H<sub>2</sub>O for ZnCdCr-LDH, respectively (Table 1).

The two LDHs we obtained have a similar XRD pattern of typical layered compounds. As the sum of the length of DS molecule (21.3 Å) and the layer thickness (about 4.8 Å) almost coincides with the spacing values (26.9 and 27.1 Å) on the basis of the XRD data [24], a monolayer of surfactant chains oriented perpendicularly and interdigitated in between the inorganic brucite-like

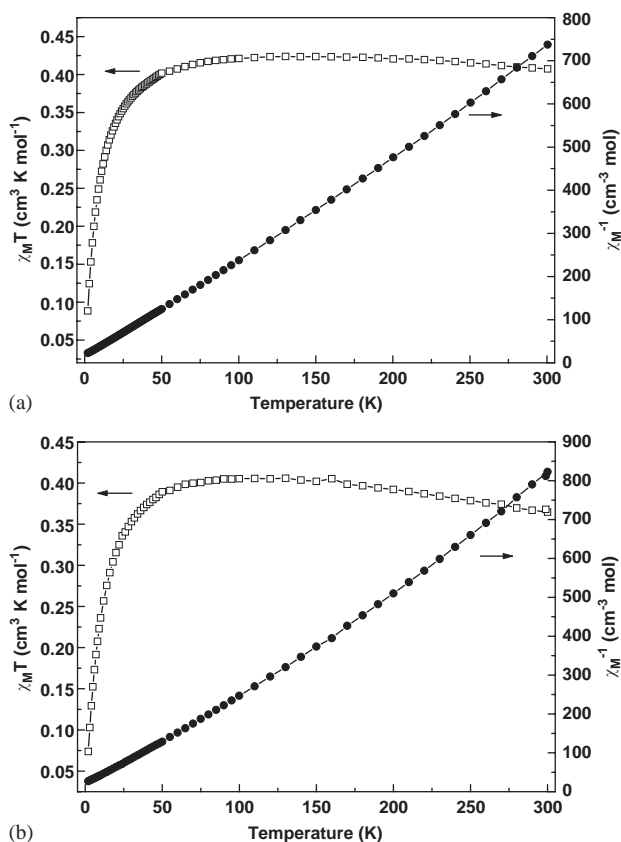


Fig. 6. Plots of the temperature dependence of  $\chi_M T$  (open squares) and  $\chi_M^{-1}$  (solid circles) for (a) CdCr-LDH and (b) ZnCdCr-LDH.

layers is envisioned (the schematic model is shown in Fig. 7). Besides the XRD patterns, the IR analysis and the thermal decomposition processes also confirm the presence of DS molecules in the two LDH materials. From the TG analysis, there is difference between the two LDHs: ZnCdCr-LDH has a higher dehydroxylation temperature and higher end temperature of weight loss in comparison with CdCr-LDH. This TG difference suggests that the introduction of zinc renders the LDH material thermally more stable. Although both CdCr-LDH and ZnCdCr-LDH have ordered layer structure, the latter seems to be more ordered than the former because the peak intensities of the XRD pattern of ZnCdCr-LDH are higher than those of CdCr-LDH. Furthermore, the ZnCdCr-LDH possesses less positive charges in the inorganic sheets than CdCr-LDH. These may contribute to the difference in thermal stability between the two samples. From the empirical compositions, it is seen that the amount of DS and hydroxyl (including water molecules) species in CdCr-LDH is about 48.9 wt% whereas that in ZnCdCr-LDH is about 55.2 wt%. These amounts reasonably correspond to the respective total weight loss values (about 46% for CdCr-LDH and about 60% for ZnCdCr-LDH) in the recorded TG curves for the two samples.

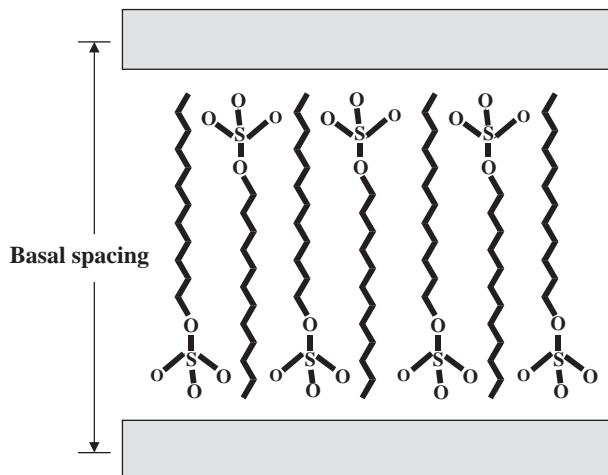


Fig. 7. Schematic model of the LDH intercalated with dodecyl sulfate.

As expected, diffuse reflectance UV-vis spectra of the two compounds show the two distinct bands attributed to  $d-d$  transitions ( $4A_{2g} \rightarrow 4T_{2g}$  and  $4A_{2g} \rightarrow 4T_{1g}$ , respectively [27–29]). These two bands indicate that the  $\text{Cr}^{\text{III}}$  species in the LDH compounds are mononuclear in a nearly octahedral  $\text{OH}^-$  environment [27,29,30], and therefore the inorganic layers in both CdCr-LDH and ZnCdCr-LDH can be described as layers of macroanionic hydroxochromate (III),  $[\text{Cr}(\text{OH})_6]^{3-}$ . In comparison with CdCr-LDH, the two absorption bands of ZnCdCr-LDH blue shift from 412 to 383 nm and from 574 to 557 nm, respectively. The blue shift is attributed to electronic competition between  $\text{Cr}^{\text{III}}$  and  $\text{M}^{\text{II}}$  ( $\text{Zn}^{\text{II}}$  and  $\text{Cd}^{\text{II}}$ ), which affects the donor ability of bridging OH groups towards the  $\text{Cr}^{\text{III}}$  ions. The UV-vis spectra indicate that the concurrence of zinc and cadmium intensifies the electronic competition between  $\text{Cr}^{\text{III}}$  and  $\text{M}^{\text{II}}$  and accordingly the  $\text{Cr}^{\text{III}}$  ion experiences a stronger ligand field in ZnCdCr-LDH than in CdCr-LDH [29].

In the temperature dependence plots of the magnetic susceptibility, the slight increase of  $\chi_M T$  with lowering temperature for the two compounds in the temperature range 130–300 K indicates the presence of a weak ferromagnetic exchange interaction [31,32] between the  $\text{Cr}^{\text{III}}$  centers. The decrease of  $\chi_M T$  for the two compounds (Fig. 6) at lower temperatures (2–130 K) results from characteristic antiferromagnetic interactions between the  $\text{Cr}^{\text{III}}$  sites together with the zero field splitting effects of  $\text{Cr}^{\text{III}}$  [33–36]. The magnetic susceptibility data of CdCr-LDH roughly follow the Curie–Weiss equation in the temperature range of 2–130 K, as there is a linear relationship between  $\chi_M^{-1}$  and T within this temperature range. And the Curie–Weiss fitting of the magnetic data for CdCr-LDH gives rise to  $C = 0.45 \text{ cm}^3 \text{ K mol}^{-1}$  and  $\theta = -6.94 \text{ K}$ . For ZnCdCr-LDH, the  $\chi_M^{-1}$  versus T plot in the low-temperature range obeys the Curie–Weiss law as well with a Curie constant ( $C$ ) of  $0.45 \text{ cm}^3 \text{ K mol}^{-1}$  and a Weiss constant ( $\theta$ ) of  $-9.01 \text{ K}$ .

The negative  $\theta$  value is also indicative of antiferromagnetic interaction [37] in the two compounds and this antiferromagnetic  $\text{Cr}^{\text{III}}\text{--Cr}^{\text{III}}$  interaction is believed to be through the oxygen atoms of  $\text{OH}^-$  groups between the  $\text{Cr}^{\text{III}}$  centers of the infinite sheet.

It is well known that exfoliation is a very important feature for layered materials because the exfoliated colloidal particles can be used as unique starting species to construct novel nanostructured materials. Although the delamination of LDHs is difficult because of the high charge density of the layers and the large particle size, some methods have been developed to make delamination of LDHs possible [38]. Recently, modification of LDHs with DS has been found to be effective for delamination because the intercalation of DS has the advantage to separate the layers, thus favoring the exfoliation process where the surfactant interacts with

an external solvent [15]. Adachi-Pagano and co-workers have reported that the delamination of a Zn–Al–DS LDH may occur through the use of alcohols under reflux conditions at 120 °C for 16 h [39]. Hibino et al. described [38,40] a new method for the delamination of LDHs with amino acid anions in polar solvents (formamide). Strong hydrogen bonding between the intercalated anions and polar solvent as well as between the solvent molecules themselves lead to the penetration of large volumes of solvent and hence rapid delamination. A further method was reported [41] in which the delamination of Mg–Al DS LDH occurred in a polar acrylate monomer with shearing and heating, and an LDH-acrylate nanocomposite was formed. Among these methods for delamination, the method described by Hibino is direct and the reaction occurs without heating or refluxing treatment. Therefore, we tried to

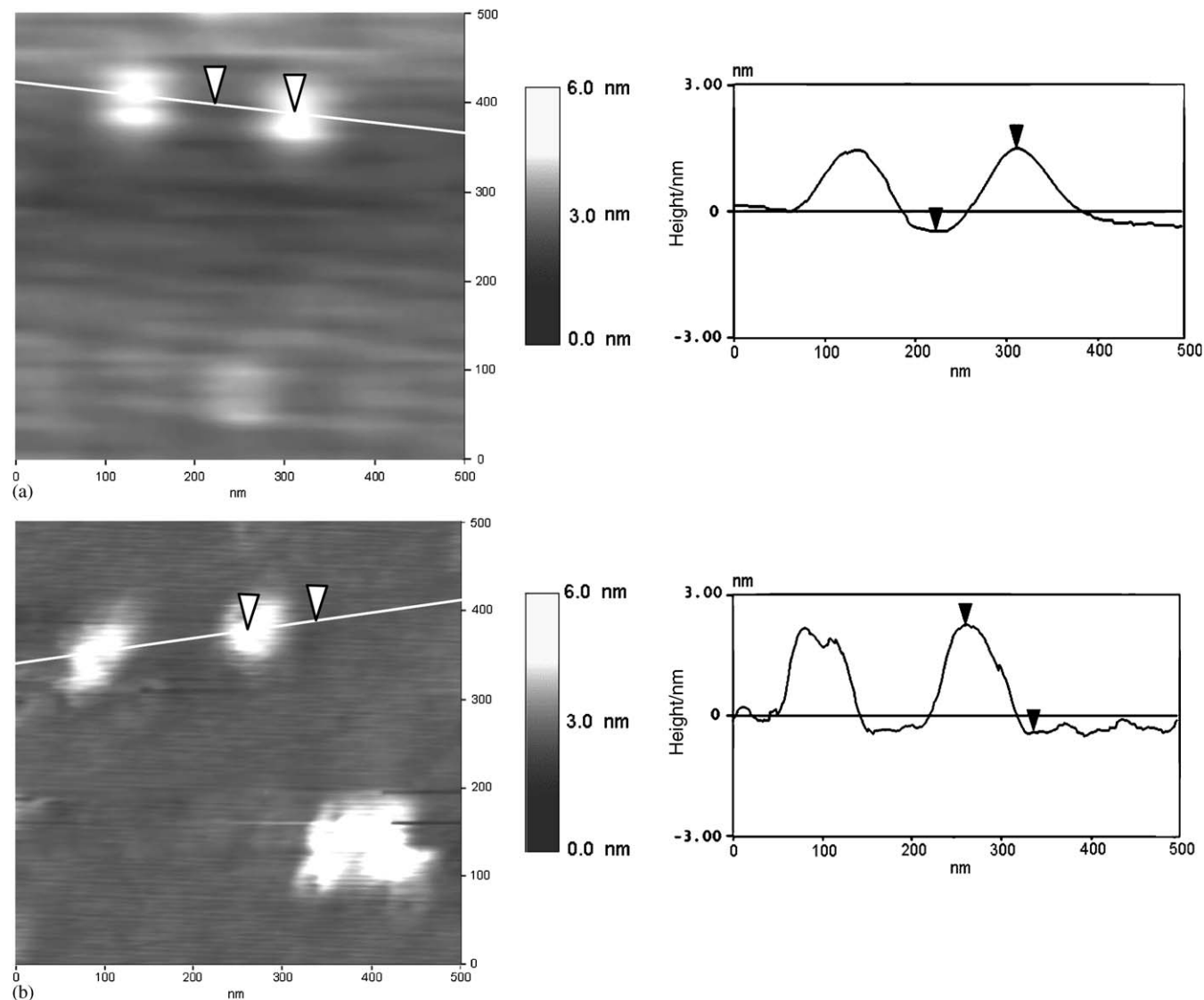


Fig. 8. AFM images of delaminated sheets on a mica substrate and height profile along the white line for (a) CdCr-LDH and (b) ZnCdCr-LDH.

disperse our compounds (CdCr-LDH and ZnCdCr-LDH) in formamide at room temperature and translucent colloidal solutions were obtained after centrifugation. The colloidal solutions, which consist of delaminated LDH portions remain stable for at least 6 months. Exfoliation of the LDH materials is evidenced by the AFM images on mica (Fig. 8). Although some aggregates consisting of a few stacked sheets show a thickness of 10–25 nm, smaller sheets with a thickness of 0.7–2.5 nm and a width of 50–100 nm are also observed. The thickness of these small sheets falls in the range between the thickness of a single inorganic layer and that of a layer consisting of the inorganic part and the DS part. Further investigation is underway to use the dispersed CdCr-LDH and ZnCdCr-LDH to prepare other composite materials with interesting properties.

## 5. Conclusions

Binary CdCr-LDH and ternary ZnCdCr-LDH with DS as the counter anion have been synthesized by a coprecipitation technique for the first time. The obtained materials show high structural order, and the introduction of the DS groups in the interlayer space of LDH is evidenced by XRD, IR, TG and elemental analysis. The UV-vis spectra reveal the existence of mononuclear state of Cr<sup>III</sup> in a nearly octahedral OH<sup>-</sup> environment within the hydroxide layer of the LDHs. From the magnetic analysis, antiferromagnetic interactions between the chromium ions are observed for the two LDHs at low temperatures. The introduction of zinc has an effect on structure and ligand field as well as Cr<sup>III</sup>–Cr<sup>III</sup> interaction in the LDH material. The two compounds can be exfoliated into single layer colloidal solutions, which may find application as starting materials to construct new nanostructured materials.

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