

## Topochemical Oxidation of Transition Metals in Layered Double Hydroxides by Anthraquinone-2-sulfonate

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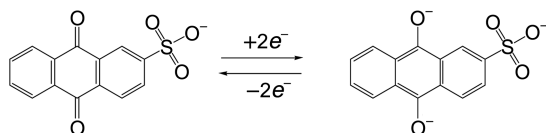
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Layered double hydroxides (LDH), also known as hydro-talcite-like clays, consist of positively charged metal hydroxides and charge balancing anions, expressed by a general formula  $[M^{2+}_{(1-x)}M^{3+}_x(OH)_2]A^{n-}_{x/n} \cdot mH_2O$ , wherein  $M^{2+}$  and  $M^{3+}$  can be any divalent and trivalent metal cations occupied in the octahedral holes of a brucite-like layer and  $A^{n-}$  is any hydrated exchangeable anion positioned in the gallery between the layers through a strong electrostatic and intermolecular interaction.<sup>1</sup> Physical and chemical properties of the LDHs could be tuned by changing the composition of the LDH host layers such as transition metals *e.g.* Co, Ni, Fe *etc.* for catalysts, electrochemical materials and magnetic precursory materials.<sup>2</sup> Especially,  $Fe^{3+}$  readily formed a gel-like  $Fe(OH)_3$  phase in an alkaline solution<sup>3</sup> and  $Fe^{2+}$ - $Fe^{3+}$  LDHs (green rust) could be obtained by an oxidation of brucite-like  $Fe(OH)_2$  in the presence of anions.<sup>4</sup> Recently, Ma *et al.* reported a two-step synthesis of  $Co^{2+}$ - $Fe^{3+}$ -LDH from  $Co^{2+}$ - $Fe^{2+}$  brucite-like hydroxides, by using hydrolysis of hexamethylenetetramine (HMT) and oxidation of  $Fe^{2+}$  by iodine.<sup>5</sup> We chose a mild oxidizing agent such as anthraquinone in order to substitute iodine and provide anionic functionality to drive the intercalation reaction in LDH layers. In this study, we developed a novel synthetic approach to hydro-talcite-like  $Co^{2+}$  (or  $Ni^{2+}$ )- $Fe^{3+}$ -LDHs using a one-pot topochemical oxidation reaction by anthraquinone-2-sulfonate anions (AQS2) (Scheme 1), in which the AQS2 allowed a sole oxidation of  $Fe^{2+}$  into  $Fe^{3+}$  to form the LDH phase and were also intercalated into the interlayer space of the LDH during the course of a slow precipitation.

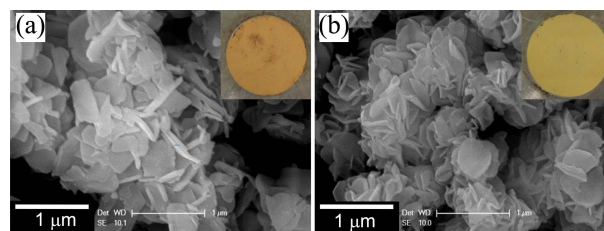
The  $Co^{2+}$  (or  $Ni^{2+}$ )- $Fe^{3+}$ -LDH was synthesized by refluxing the  $CoCl_2$  (or  $NiCl_2$ )- $FeCl_2$ -AQS2-HMT solution with stoichiometric ratio 2:1 of Co (or Ni):Fe under  $N_2$  atmosphere for 3 hours. Refluxing the mixtures yielded brown



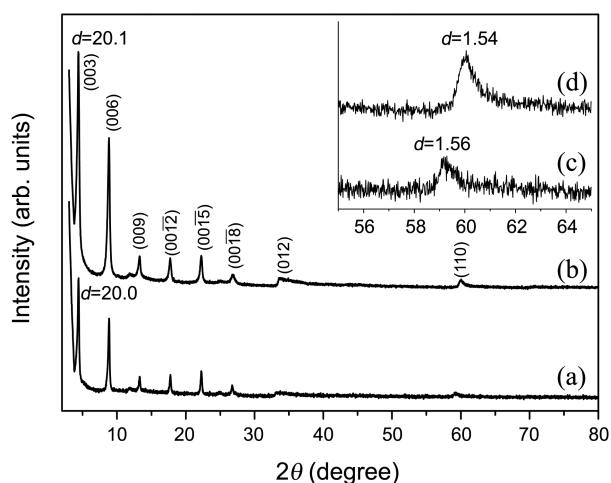
**Scheme 1.** Two electron reduction and oxidation process of anthraquinone-2-sulfonate.

colored solid precipitates for the Co-Fe-LDH and dark yellow for the Ni-Fe-LDH, respectively, as shown in the insets of Figure 1. The color of the starting  $CoCl_2$ - $FeCl_2$  solution was pink due to colorless ferrous ions dissolved. After refluxing with the AQS2, the pink color of the solution changed to a brownish one, suggesting the existence of ferric ions, and finally the brown solid precipitates were yielded. Without the AQS2, pink colored precipitates of brucite-like  $Co^{2+}$ - $Fe^{2+}$  hydroxides were obtained as mentioned in a previous report.<sup>5</sup> The results strongly suggest that the redox reactions between  $Fe^{2+}$  and AQS2 have been involved in the coprecipitation by the HMT hydrolysis. The oxidation potential of AQS2<sup>2-</sup>/AQS2 was measured as  $-0.60$  V (vs Ag/AgCl),<sup>6</sup> which is probably capable of oxidizing the  $Fe^{2+}$  ions in  $Fe(OH)_2$  phase because of  $+0.58$  V of standard oxidation potential in  $Fe(OH)_3/Fe(OH)_2$ .<sup>7</sup> According to our previous report for hydro-talcite-like  $\alpha$ -cobalt hydroxide containing AQS2,<sup>8</sup> the AQS2 did not oxidize the  $Co^{2+}$  ions under similar reaction conditions. In the present study,  $Fe^{2+}$  was oxidized into  $Fe^{3+}$ , resulting in the  $Co^{2+}$ - $Fe^{3+}$  hydroxide layers forming the LDH structures. Figure 1 shows typical SEM images of the Co-Fe-LDH and the Ni-Fe-LDH samples, consisting of uniform platelets with an average lateral size of  $0.5 \mu m$  and a thickness of  $\sim 70$  nm for both samples. Well-crystallized LDH platelets in SEM inspections further revealed little impurity such as gel-like  $Fe(OH)_3$  phase, often observed in alkaline solution syntheses in the presence of oxygen.<sup>4</sup>

Figure 2 shows typical XRD patterns of the Co-Fe-LDH and the Ni-Fe-LDH products. All diffraction peaks were



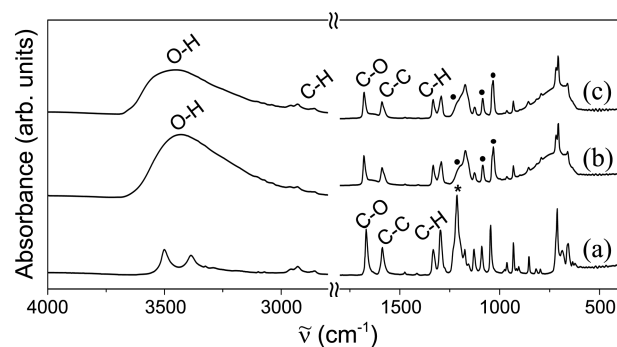
**Figure 1.** SEM images of (a)  $Co^{2+}$ - $Fe^{3+}$ -LDH and (b)  $Ni^{2+}$ - $Fe^{3+}$ -LDH powders. Insets show photographs of each sample.



**Figure 2.** XRD patterns of (a)  $\text{Co}^{2+}\text{-Fe}^{3+}$ -LDH and (b)  $\text{Ni}^{2+}\text{-Fe}^{3+}$ -LDH. The (c) and (d) are enlarged XRD patterns ranging from  $55^\circ$  to  $65^\circ$  in  $2\theta$ . Unit of the  $d$  values is Å.

readily indexed as a hydrotalcite-like phase similar to those in  $\alpha$ -Co-AQS2-LDH phase.<sup>8</sup> The XRD patterns indicate the characteristic reflections of a well-oriented LDH structure due to the series of high order (00 $l$ ) reflections. The LDH phases were confirmed and the refined lattice parameters were  $c = 60.0$  Å and  $a = 3.12$  Å ( $a = 2d_{110}$ ) for the Co-Fe-LDH, and  $c = 60.3$  Å and  $a = 3.08$  Å for the Ni-Fe-LDH, respectively. The slightly larger  $a$  axis of the Co-Fe-LDH than that of the Ni-Fe-LDH might be considered to result from the different ionic radii of  $\text{Co}^{2+}$  (73.5 pm) and  $\text{Ni}^{2+}$  (69 pm). The  $a$  axes for those two LDH phases are very similar to  $a = 3.12$  Å in  $\text{Co}_2\text{Fe-LDH}$ <sup>5</sup> and to  $a = 3.078$  Å in  $\text{Ni}_2\text{Fe-LDH}$ .<sup>9</sup> They are also smaller than  $a = 3.17$  Å<sup>4a</sup> of  $\text{Fe}^{2+}\text{-Fe}^{3+}$ -LDH. This revealed the successful formation of the Co(or Ni)<sub>2</sub>-Fe-LDH phases and also suggested a random occupation of the ferric ions into the metal sites of the LDH structure. Moreover, sharp reflections in the XRD patterns of the both samples reveal a high crystallinity of the LDH hosts as well as a preferred orientation of the interlayer AQS2. A basal spacing of 20.1 Å for the Co-Fe-LDH gives an effective separation of 15.4 Å to accommodate the AQS2, assuming a 4.6 Å thickness for  $\text{Co}_2\text{Fe}$ -hydroxide layer,<sup>5</sup> with an antiparallel arrangement that might be ascribed to a strong intermolecular interaction of the AQS2 being self-assembled in the interlayer spaces of LDH. The attraction of the AQS2 is believed to lead to successful co-precipitation of the  $\text{Co}^{2+}$  (or  $\text{Ni}^{2+}$ ) and  $\text{Fe}^{2+}$  into the single brucite-like phase involving the sole oxidation of  $\text{Fe}^{2+}$  into  $\text{Fe}^{3+}$  in the hydroxide frames under the HMT hydrolysis. The structural deformation of the hydroxide layers during the topochemical oxidation was minimized since the AQS2 remained in their interlayer spaces acting as guest molecules.

FT-IR spectra in Figure 3 exhibited the characteristic absorption features of the Co-Fe and Ni-Fe hydroxide and the intercalated AQS2. The large broadband at  $3500\text{ cm}^{-1}$  was assigned to overlapping stretching modes of hydroxyl groups both in the hydroxide layers and the interlayer water molecules.<sup>11</sup> The bands below  $600\text{ cm}^{-1}$  were associated



**Figure 3.** FT-IR spectra of (a) anthraquinone-2-sulfonate sodium salt, (b)  $\text{Co}^{2+}\text{-Fe}^{3+}$ -LDH and (c)  $\text{Ni}^{2+}\text{-Fe}^{3+}$ -LDH. Black circles and asterisk indicate characteristic peaks of sulfonate group in AQS2.

with metal-oxygen stretching and metal-hydroxide bending vibrations. The strong vibration band observed at around  $1678\text{ cm}^{-1}$  was assigned to C=O stretching mode in the AQS2 guests. The peaks at  $1589\text{ cm}^{-1}$  corresponded aromatic C=C stretching mode and others at  $1331$  and  $1292\text{ cm}^{-1}$  to aromatic C-H stretching modes, respectively. The peaks at  $1205$  (broad),  $1085$ , and  $1033\text{ cm}^{-1}$  were attributed to asymmetrical and symmetrical stretching modes of interlayer sulfonate groups, respectively.<sup>10</sup> S-O stretching bands in  $\text{SO}_3^-$  were shifted from  $1213$  (sharp, asymmetric mode) and  $1045\text{ cm}^{-1}$  (sharp, symmetric mode) in the sodium salt to  $1205$  (broad) and  $1033\text{ cm}^{-1}$  (sharp) in LDH structure. The reduced intensities in  $1205\text{ cm}^{-1}$  of the LDH samples dominantly indicate the possible intercalation of AQS2 into the interlayer spaces of LDH. The absorbance due to carbonate anion intercalation was not detected by FT-IR spectroscopy.

In summary, highly crystalline  $\text{Co}^{2+}$  (or  $\text{Ni}^{2+}$ )- $\text{Fe}^{3+}$ -LDHs have been synthesized using a unique topochemical oxidation process by AQS2, which also functioned as intercalative moieties during a course of homogeneous precipitation of the metal hydroxides. The AQS2 played a key role in the oxidative intercalation process to produce the highly crystalline  $\text{Fe}^{3+}$ -containing LDHs. A strong intermolecular interaction of the AQS2 guests in the interlayer spaces of LDH could prevent a structural deformation of the crystalline hydroxide layers during the oxidation process of  $\text{Fe}^{2+}$ . This synthetic strategy could be extended to prepare other important series of transition-metal LDHs in various  $\text{M}^{2+}/\text{Fe}^{3+}$  ratios such as  $\text{Co}^{2+}\text{-Fe}^{2+}\text{-Fe}^{3+}$ -LDH,  $\text{Ni}^{2+}\text{-Fe}^{2+}\text{-Fe}^{3+}$ -LDH and  $\text{Fe}^{2+}\text{-Fe}^{3+}$ -LDH for pure spinel ferrites.

## Experimental

**Synthesis of  $\text{M}^{2+}(\text{Co}^{2+}, \text{Ni}^{2+})\text{Fe}^{3+}$ -LDH-AQS2.** Crystalline samples were synthesized involving the precipitation from aqueous solutions of divalent cobalt (or nickel) and ferrous ions through HMT hydrolysis by refluxing in a nitrogen gas.  $\text{Co(II)Cl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Fe(II)Cl}_2 \cdot 4\text{H}_2\text{O}$  and anthraquinone-2-sulfonic acid sodium salt were dissolved in a degassed and deionized water. This solution was purged by nitrogen gas for 2 hr to expel oxygen from the solution, then a HMT was introduced into the solution, which contains 5.0 mM of

CoCl<sub>2</sub>, 2.5 mM of FeCl<sub>2</sub>, 5 mM of AQS2 and 60 mM of HMT respectively. The solution was heated at refluxing temperature under continuous magnetic stirring and nitrogen gas protection for 3 hr. Brown (for Co<sup>2+</sup>-Fe<sup>3+</sup>-LDH) and dark-yellow (for Ni<sup>2+</sup>-Fe<sup>3+</sup>-LDH) colored products were recovered by a filtration, then washed with water and ethanol several times.

**Characterization.** X-Ray diffraction (XRD) data were collected on a Philips PANalytical X'pert pro diffractometer with CuK<sub>α</sub> radiation with  $\lambda = 1.542 \text{ \AA}$ , 40 kV, 40 mA. Fourier-transform infrared spectroscopy (FT-IR) spectra for powder were recorded on a Biorad FTS 6000 FT-IR Spectrometer equipped with a high performance DuraSamplIR II diamond accessory of attenuated total reflectance (ATR) mode in the range of 400-4000 cm<sup>-1</sup> with 100 scans at 4 cm<sup>-1</sup> resolution and the photovoltaic liquid cooled mercury-cadmium-telluride (MCT) detector. Scanning electron microscopy (SEM) images were taken on JSM 840F at 25 kV.

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