

Topochemical Synthesis of Monometallic (Co^{2+} – Co^{3+}) Layered Double Hydroxide and Its Exfoliation into Positively Charged $\text{Co}(\text{OH})_2$ Nanosheets**

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Lamellar cobalt hydroxide has attracted much attention in applications of catalysts, adsorbents, and high-performance electrochemical materials.^[1] In particular, cobalt hydroxide can be used as an important additive to improve the electrochemical activity of alkaline secondary batteries or as a potential candidate material for electrochemical supercapacitors.^[2] There has also been remarkable interest in the long-range magnetic ordering of cobalt hydroxide, whereby attempts to incorporate organic groups into the interlayer spaces to form organic–inorganic magnetic materials have been reported.^[3] A study on the ferromagnetic layered cobalt hydroxysulfate has demonstrated a purely 2D magnetic ordering.^[3c] It is known that lamellar cobalt hydroxide can be crystallized into a hexagonal structure with two polymorphs, α and β .^[4] The β phase, also known as a brucite-like form of $\text{Co}(\text{OH})_2$, possesses charge-neutral edge-sharing octahedral layers of divalent cobalt cations that are sixfold coordinated by hydroxy ions. In contrast to the anion-free structure in β - $\text{Co}(\text{OH})_2$, the α phase exhibits an expanded interlayer spacing with anions (CO_3^{2-} , NO_3^- , Cl^- , etc.) residing in the gallery.^[5] Previous structure assumptions suggested a possibility that the α - $\text{Co}(\text{OH})_2$ phase might be isostructural with hydrotalcite-like layered double hydroxide (LDH),^[6] that is, $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]^+[\text{A}^{n-}_{x/n}]^{x-m}\text{H}_2\text{O}$ (A: counterions), comprising octahedral host layers of $\text{Co}^{2+}/\text{Co}^{3+}$. However, detailed structural analyses have recently identified the α phase as a hydroxy salt, signified by the absence of Co^{3+} , instead of incorporation of a portion of tetrahedrally coordinated Co^{2+} centers above and below the octahedral host layers.^[7] The anions occupy the tetrahedral fourth apex pointing into the interlayer space, and are not as easily exchangeable at room temperature as the counterions in an LDH structure. Highly crystalline α - $\text{Co}(\text{OH})_2$ and β - $\text{Co}(\text{OH})_2$ are now readily available owing to recent synthetic progress.^[8] Both compounds, as a result of the overall charge-neutral host layers and lack of counterions, do not possess a

desirable anion-exchange capacity, thus hindering the exploration of intercalation chemistry, modification of guest anionic species, and exfoliation into unilamellar sheets.

Recent interest in the newly discovered superconducting CoO_2 layers has provided an excellent example of the importance of modifying and controlling the oxidation state of a transition metal ($\text{Co}^{3+}/\text{Co}^{4+}$) in a 2D layer.^[9] One such instance of valence engineering could be exploited in lamellar cobalt hydroxide, for example, to achieve a monometallic LDH phase ($\text{Co}^{2+}/\text{Co}^{3+}$), and might offer prospects for probing intriguing new electronic and magnetic properties and may produce a meaningful comparison with their superconducting oxide counterparts. Furthermore, if such a monometallic LDH phase could be exfoliated as other traditional Al^{3+} -based phases,^[10] it would provide, for the first time, a molecular layer of monometallic hydroxides in an ultimate two-dimensional anisotropy and charge-bearing form. These positively charged unilamellar nanosheets may be used as building blocks in constructing new functional ultrathin films, molecular heteroassemblies, and composite nanostructures.^[11] However, no stable dissociated Co^{3+} or $\text{Co}(\text{OH})_3$ compound exists in aqueous solution since Co^{3+} is a very strong oxidizing agent.^[12] Therefore, conventional methods of preparing LDHs through coprecipitation^[13] or homogeneous precipitation^[14] are not applicable as these methods require the precipitation from solutions of mixed Co^{2+} and Co^{3+} ions. It is apparent that a new synthetic strategy has to be developed for a Co^{2+} – Co^{3+} LDH phase.

We have recently demonstrated an innovative topochemical approach for transforming bimetallic brucite-like Co^{2+} – Fe^{2+} hydroxides ($\text{Co}_{2/3}\text{Fe}_{1/3}(\text{OH})_2$) into hydrotalcite-like Co^{2+} – Fe^{3+} LDH ($\text{Co}_{2/3}\text{Fe}_{1/3}(\text{OH})_2\text{I}_{1/3}$) that is based on the rational control of oxidation states of different transition metals.^[15] The same principle of topochemical conversion and valence control might also be adopted to produce monometallic Co^{2+} – Co^{3+} LDH. Different from the case for heterometallic (Co–Fe) hydroxide, more crucial control has to be accomplished on the degree of oxidation by incorporating mixed valences for the same metal. Herein, we present a new topochemical route for transforming β - $\text{Co}(\text{OH})_2$ into a Co^{2+} – Co^{3+} LDH phase with a typical $\text{Co}^{2+}/\text{Co}^{3+}$ ratio of 2:1 through an oxidative intercalation process employing bromine (Br_2) in acetonitrile (CH_3CN). This transformation is the first example of achieving a highly crystalline LDH phase based on a sole transition metal with mixed oxidation states. The synthesized Co^{2+} – Co^{3+} LDHs, upon exfoliation in formamide, provide positively charged nanosheets of $\text{Co}(\text{OH})_2$, the

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ultimate two-dimensional building block for monometallic hydroxides.

Heating a solution of CoCl_2 and hexamethylenetetramine (HMT) at reflux yielded pink-colored solid precipitates, which SEM images showed to be highly developed hexagonal platelets (Figure 1). The hexagonal platelets exhibit an average lateral size of 3–4 μm and a thickness of a few tens

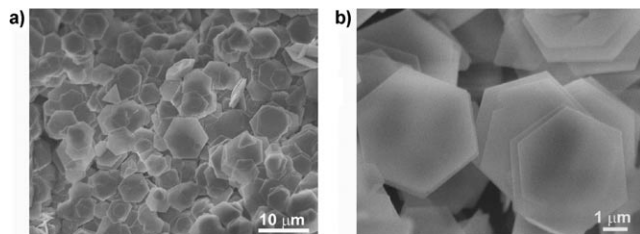


Figure 1. a, b) SEM images of as-prepared $\beta\text{-Co(OH)}_2$.

of nanometers. A typical XRD pattern of the product is shown in Figure 2a (I). All the diffraction peaks are well indexed as a brucite-like phase with refined lattice parameters

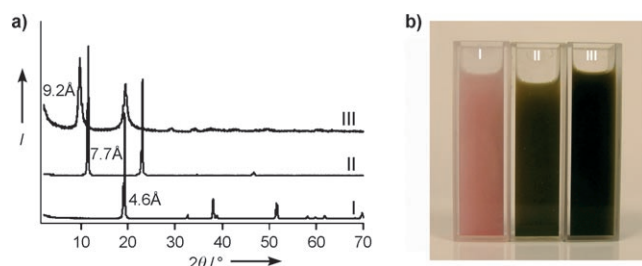
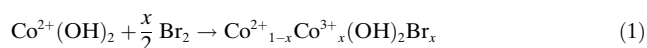


Figure 2. a) XRD patterns associated with the topochemical transformations. b) Suspensions of as-prepared products dispersed in ethanol. In both panels: I) $\beta\text{-Co(OH)}_2$; II) $\text{Co}^{2+}\text{-Co}^{3+}$ LDH after treatment with $\text{Br}_2/\text{CH}_3\text{CN}$; III) ClO_4^- -intercalated $\text{Co}^{2+}\text{-Co}^{3+}$ LDH.

of $a = 3.176(2) \text{ \AA}$ and $c = 4.643(2) \text{ \AA}$, which are in good agreement with our previous data on single-crystal platelets of $\beta\text{-Co(OH)}_2$.^[8] After being treated with $\text{Br}_2/\text{CH}_3\text{CN}$, the color of the sample changed from pink to blackish-brown. Photographs of the suspensions obtained by dispersing $\beta\text{-Co(OH)}_2$ and the transformed product in ethanol are shown in Figure 2b (I and II), and demonstrate an obvious color change during the transformation. As given in Figure 2a (II), the basal spacing of the blackish-brown sample expanded to about 7.7 $\text{\AA}$, indicating possible transition to an anion-intercalated phase, which is in striking contrast to the starting anion-free $\beta\text{-Co(OH)}_2$ phase. The interlayer spacing (7.7 $\text{\AA}$) fits well with a hydrotalcite-like LDH phase with Br^- ions as counteranions.^[16] Oxidation of the divalent cobalt species to a trivalent state and resultant intervalence transition likely give rise to the blackish color of the transformed product. A redox reaction seems to take place in the phase change [Eq. (1)].



The question then turns to how much bromine should be introduced and how much Co^{2+} is oxidized? According to Equation (1), the extent of oxidation seems to be theoretically determined by the amount of bromine used. Specifically, oxidizing $\frac{1}{3} \text{ mol Co}^{2+}$ to Co^{3+} and forming a 2:1 ratio of $\text{Co}^{2+}/\text{Co}^{3+}$ requires an x value of $\frac{1}{3} \text{ mol}$, that is, $\frac{1}{6} \text{ mol Br}_2$. In our practical experiments, however, we found it mandatory to use more than the required amount of bromine. Based on experimental findings (see Figure S1 in the Supporting Information), a typical oxidative intercalation procedure has been designed with 40 times the required amount of Br_2 and with treatment duration of about five days to ensure complete conversion into a single $\text{Co}^{2+}\text{-Co}^{3+}$ LDH phase without residual $\beta\text{-Co(OH)}_2$.

The exact valence number of Co in the transformed LDH was determined by chemical analysis to be 2.34, which indicates that only one-third of the Co^{2+} species in $\beta\text{-Co(OH)}_2$ were oxidized even with the use of excess bromine (ca. 40 times) and long treatment time (ca. 5 days). This result seems surprising but reveals an important discovery that the conversion from $\beta\text{-Co(OH)}_2$ into a $\text{Co}^{2+}\text{-Co}^{3+}$ LDH might be governed by both kinetic and thermodynamic factors. From a kinetic point of view, an abundance of bromine and prolonged treatment are beneficial in completing the transformation. Thermodynamically, a 2:1 $\text{Co}^{2+}/\text{Co}^{3+}$ LDH phase reached by oxidizing one-third of the total Co^{2+} ions may be considered as the most stable and favorable structure. The reason for the thermodynamic stability could be ascribed to a reasonable assumption whereby direct neighboring of Co^{3+} to other Co^{3+} ions may be energetically unfavorable. In a 2:1 $\text{Co}^{2+}/\text{Co}^{3+}$ ratio, the positioning of Co^{3+} ions as nearest neighbors in the trigonal (hexagonal) host lattice can be avoided (see Figure S3 in the Supporting Information). The chemical composition of the obtained Br^- -intercalated product was estimated to be $\text{Co}^{2+}_{0.66}\text{Co}^{3+}_{0.34}(\text{OH})_2\text{Br}_{0.34} \cdot 0.4\text{H}_2\text{O}$ (calcd elemental analysis (%): Co 46.3, Br 21.3; calcd ignition loss (%): 41.1; calcd Co valence: 2.34; elemental analysis (%) found: Co 46.96, Br 21; ignition loss found (%): 40.8; Co valence found: 2.34). Lattice refinement resulted in a rhombohedral unit cell of the converted Br^- -intercalated $\text{Co}^{2+}\text{-Co}^{3+}$ LDH with parameters $a = 3.110(5) \text{ \AA}$ and $c = 23.18(4) \text{ \AA}$.

Figure 3a,b displays SEM images of the transformed $\text{Co}^{2+}\text{-Co}^{3+}$ LDH. It can be seen that the size, shape, and morphology of the transformed products are essentially the same as those of the precursor $\beta\text{-Co(OH)}_2$ crystals. Employing an elemental mapping technique in the transmission electron microscope, spatial elemental profiles of the platelets are visualized in Figure 3c. A homogeneous distribution of cobalt and bromine atoms across the hexagonal platelet reveals the incorporation of bromine for the converted Br^- -intercalated $\text{Co}^{2+}\text{-Co}^{3+}$ LDH and an undoubtedly genuine topotactic nature of the redox reaction.

The obtained Br^- -intercalated LDH was converted by anion exchange into a ClO_4^- form by treatment with sodium perchlorate (NaClO_4) and dilute HCl solution. After ultrasonically dispersing as-exchanged ClO_4^- LDHs in formamide, the occurrence of delamination was observed. The morphology and size of the exfoliated nanosheets were examined by

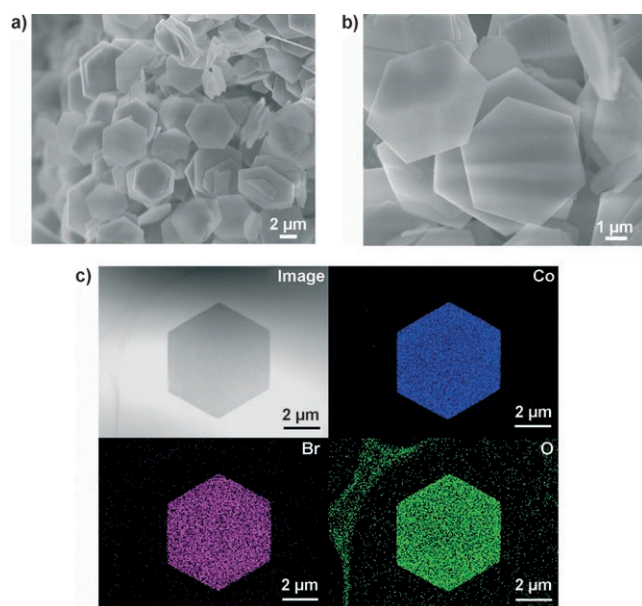


Figure 3. a, b) SEM images of Br^- -intercalated Co^{2+} – Co^{3+} LDHs. c) Corresponding elemental maps of Co, Br, and O in a Br^- -intercalated Co^{2+} – Co^{3+} LDH platelet.

AFM. A tapping-mode AFM image in Figure 4a shows sheetlike objects with extremely small thickness and lateral dimensions of several hundred nanometers, coexisting with some nanoparticles of several or tens of nanometers. In contrast to the parent hexagonal crystallites, the nanosheets

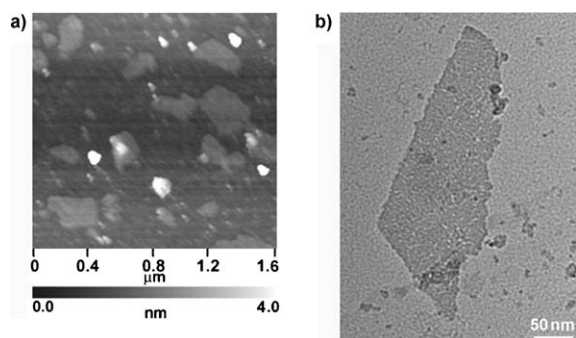


Figure 4. Co^{2+} – Co^{3+} LDH nanosheets: a) AFM image; b) TEM image.

are irregular in shape, indicating severe fracturing during the delamination process. An average thickness of 0.8 nm was evaluated for the nanosheets, which is very close to that previously observed for other LDH nanosheets.^[10,15] A typical TEM image shown in Figure 4b also shows a nanosheet with very faint contrast. The lateral dimension of several hundred nanometers implies that they might be derived from the same objects that were identified by AFM. These observations thus confirm that the obtained Co^{2+} – Co^{3+} LDH nanosheets are of unilamellar nature. In other words, they are molecular layers of $\text{Co}(\text{OH})_2$ with positive charges, which may be regarded as an ultimate form of metal hydroxide composed of a sole transition metal with mixed valences $[(\text{Co}^{2+}_{0.66}\text{Co}^{3+}_{0.34}(\text{OH})_2)^{0.34+}]$.

In conclusion, we report a topochemical route for transforming brucite-like $\beta\text{-Co}(\text{OH})_2$ into a monometallic Co^{2+} – Co^{3+} LDH. The designated oxidative intercalation process, employing bromine in acetonitrile, causes oxidation of $\frac{1}{3}$ Co^{2+} into Co^{3+} while intercalating Br^- as charge-balancing counteranions. Experimental data revealed that the LDH host layer thermodynamically adopts a 2:1 ratio of $\text{Co}^{2+}/\text{Co}^{3+}$ for possible avoidance of nearest neighboring of the Co^{3+} ions regardless of excessive use of the oxidizing agent. This is the first example of achieving a highly crystalline LDH phase that is based on a single transition metal with mixed valences. It demonstrates a vital concept of rationally designing and controlling the oxidation state of a transition metal in a hydroxide layer, that is, by valence engineering. It also offers a possible meaningful comparison with other layered cobalt hydroxy salts and superconducting CoO_2 counterparts. Furthermore, as-obtained Co^{2+} – Co^{3+} LDHs, after ion exchange to give the perchlorate form, could be exfoliated into unilamellar nanosheets in formamide. These positively charged molecular layers of $\text{Co}(\text{OH})_2$ may hold great potential, for example, in functional ultrathin films/coatings, nanocomposites, and electromagnetic devices.

Experimental Section

Pink-colored $\beta\text{-Co}(\text{OH})_2$ was synthesized by a similar process to that described previously (see the Supporting Information for details).^[8] As-prepared $\beta\text{-Co}(\text{OH})_2$ (0.45 g) was dispersed and stirred with a magnetic stirbar in $\text{Br}_2/\text{CH}_3\text{CN}$ solution (5 g/500 mL) in an air-tight capped flask at room temperature for about 5 days. A blackish-brown product, identified as Br^- -intercalated Co^{2+} – Co^{3+} LDH, was collected by filtering and repeated washing with acetonitrile until the filtrate appeared colorless.

A portion of the blackish-brown product (0.5 g) was dispersed into a carefully degassed aqueous solution (500 mL) containing 2.5 M NaClO_4 and 2.5 mM HCl for the conversion into ClO_4^- LDH (the addition of HCl is found to be crucial for preventing carbonate (CO_3^{2-}) contamination from the air). After purging with nitrogen gas, the reaction vessel was tightly capped and shaken for 1 day at room temperature. The sample was filtered, washed with degassed water, and air-dried. Obtained ClO_4^- LDH (0.1 g) was mixed with formamide (100 mL) in a conical beaker. A translucent colloidal suspension was obtained after ultrasonic treatment for 30 min. The suspension was further centrifuged at 1000 rpm for 5 min to remove possible non-exfoliated particles.

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