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# Topochemical Synthesis, Anion Exchange, and Exfoliation of Co−Ni Layered Double Hydroxides: A Route to Positively Charged Co−Ni Hydroxide Nanosheets with Tunable Composition

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This paper describes the topochemical synthesis of Co−Ni layered double hydroxides (LDHs) from brucite-like Co−Ni hydroxides through a novel oxidative intercalation process employing bromine as an oxidizing agent, and their exfoliation into positively charged unilamellar nanosheets in formamide after anion-exchange treatment. In this protocol, hexagonal microplatelets of brucite-like Co−Ni hydroxides in variable composition were prepared by homogeneous precipitation of a mixed solution of divalent cobalt and nickel ions via hexamethylenetetramine hydrolysis. Subsequent treatment of the brucite-like Co−Ni hydroxides with excessive bromine in acetonitrile promoted partial oxidation of $Co^{2+}$ into $Co^{3+}$, producing $Br^-$-intercalated Co−Ni LDHs inheriting the hexagonal morphology. This rational topochemical approach was applicable for realizing a pure phase of Co−Ni LDHs with nickel content up to 50% (metal content). Chemical analyses indicated that as-prepared Co−Ni−Br LDHs were unexceptionally characterized by a general chemical formula as $[(Co^{2+}{}_{1-3x/2}Ni^{2+}{}_{3x/2})_{2/3}Co^{3+}{}_{1/3}(OH^-)_2][Br^-{}_{1/3}\cdot 0.5H_2O]$ ($x \leq 0.5$), a thermodynamically stable LDH structure with a $M^{2+}/M^{3+}$ ratio of 2:1. We developed an ethanol-assisted anion-exchange approach, which was effective in preventing carbonate contamination in preparing a variety of inorganic and organic anionic forms of Co−Ni LDHs. As-prepared $NO_3^-$ intercalated Co−Ni LDHs without substantial carbonate contamination were successfully exfoliated into unilamellar nanosheets bearing positive charges upon contact with formamide. The translucent nanosheet suspensions exhibited characteristic colors depending on the variable Co/Ni ratio.

## Introduction

Layered double hydroxides (LDHs) are a family of inorganic layered materials consisting of positively charged brucite-like host layers and charge-balancing interlayer anions.[1] The wide application of LDH compounds in areas such as catalysis,[2] separation,[3] electrochemistry, and biotechnology[4,5] have attracted continuous interest from both academic and industrial fields. Recent reports demonstrate that LDH crystals can be artificially exfoliated into macromolecular nanosheets through soft-chemical procedures.[6−8] This new type of nanosheet, characterized by ultimate two-dimensional anisotropy and positive charge, is expected to exhibit distinctive physical or chemical properties associated with its extremely small thickness. The LDH nanosheets can also be

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employed as functional building blocks to produce nanodevices or superlattice-like films.[7b,9,10]

Preparing highly crystallized LDH samples is an essential requirement for investigating their fundamental physicochemical properties and for achieving well-defined nanosheets. For the most studied $Al^{3+}$-based LDHs, well-developed microplatelets can be conveniently prepared via homogeneous precipitation.[7,11] On the other hand, non-$Al^{3+}$- based LDHs, especially those composed of transition-metal elements (Fe, Co, Ni) with intriguing magnetic, electronic, and catalytic properties, are much less explored because high-quality corresponding samples are difficult to prepare. The homogeneous precipitation method cannot be applied because of difficulty in controlling the oxidation state of the metal ions in the process. Recently, we demonstrated a new oxidative intercalation approach whereby hydrotalcite-like $Co^{2+}{}_{2/3}-Fe^{3+}{}_{1/3}$ LDHs are topochemically produced from brucite-like $Co^{2+}{}_{2/3}-Fe^{2+}{}_{1/3}$ hydroxides employing iodine as an oxidizing agent in chloroform.[8a] This rational synthetic strategy has been successfully extended to produce a new monometallic $Co^{2+}{}_{2/3}-Co^{3+}{}_{1/3}$ LDHs.[8b] The $Co^{2+}{}_{2/3}-Fe^{3+}{}_{1/3}$ and $Co^{2+}{}_{2/3}-Co^{3+}{}_{1/3}$ LDHs thus obtained are well-crystallized into hexagonal-shaped microplatelets, indicating their much higher quality compared with corresponding samples thus far prepared via the conventional coprecipitation route. Significantly, chemical analyses indicate that the $Co^{2+}{}_{2/3}-Fe^{3+}{}_{1/3}$ and $Co^{2+}{}_{2/3}-Co^{3+}{}_{1/3}$ LDHs have the same host layer charge with the $M^{2+}/M^{3+}$ ratio at 2:1 ($M^{2+} = Co^{2+}$, $M^{3+} = Fe^{3+}$ or $Co^{3+}$ for $Co^{2+}{}_{2/3}-Fe^{3+}{}_{1/3}$ and $Co^{2+}{}_{2/3}-Co^{3+}{}_{1/3}$ LDHs, respectively). Because functionalities of LDHs are greatly affected by the composition, or more specifically, the host layer charge, it is important to understand the mechanism of this topochemical reaction as well as the factors governing the host layer charge of as-synthesized LDH compounds. In this regard, it is necessary to expand the topochemical conversion approach to a library of LDH compounds with a wide range of composition. Bimetallic Co−Ni hydroxide compounds are isostructural with brucite-like cobalt hydroxides, which have been prepared via various methods including coprecipitation, electroprecipitation or homogeneous precipitation.[12] Compared with Co−Fe hydroxides, Co−Ni hydroxides are air-stable and can crystallize in a brucite-like phase with continuously variable Ni content; these features make them suitable for studying the topotactic nature of the oxidative intercalation reaction and for gaining insight into the mechanism. Although nickel-rich Co−Ni LDHs have been prepared from cobalt-substituted nickelate by applying the chimie douce reaction,[13] the synthesis of Co−Ni LDHs with well-developed morphology has not yet been realized. Highly crystallized Co−Ni LDHs are desirable for achieving unilamellar Co−Ni hydroxide nanosheets through exfoliation, which may provide an effective way to improve their electrochemical and catalytic performance. Therefore, applying the oxidative intercalation approach to the Co−Ni hydroxides is of great importance.

On the other hand, anion-exchange post treatment is another indirect route to achieving LDH compounds intercalated with a wide range of inorganic and organic guests.[1,3,7] This soft-chemical method is versatile but often is accompanied by the carbonate contamination involved during the procedure. Because carbonate anions have high affinity to the host slabs,[1d] the interlayer chemistry of the LDH compounds is influenced by the degree of carbonate pollution. Especially in the case of $Co^{2+}{}_{2/3}-Fe^{3+}{}_{1/3}$ and $Co^{2+}{}_{2/3}-Co^{3+}{}_{1/3}$ LDHs, the carbonate contamination was so severe that their anion exchange and succeeding exfoliation were seriously affected.[8] Accordingly, to fully understand the interlayer properties of LDH compounds and use them for further applications, effective anion-exchange protocols must be developed to prepare carbonate-free LDH samples.

In the present study, we apply the oxidative intercalation approach to the synthesis of bimetallic Co−Ni LDHs. Highly crystallized microplatelets of Co−Ni LDHs with variable Ni content (up to 50%, metal content) were attained by topochemical transformation of brucite-like Co−Ni hydroxides with bromine. An ethanol-assisted anion-exchange approach was developed to prepare Co−Ni LDHs with minimum carbonate contamination for exfoliation into unilamellar nanosheets.

## Results and Discussion

**Topochemical Oxidation to $Co_{2/3}-Ni_{1/3}$ LDHs and Their Exfoliation.** Refluxing a solution containing $CoCl_2-NiCl_2-HMT$ ($Co^{2+}/Ni^{2+}$ molar ratio at 2:1, HMT: hexamethylenetetramine) under $N_2$ atmosphere yielded light-pink colored precipitate (abbreviated as $Co_{2/3}-Ni_{1/3}$ hydroxides). The XRD peaks (Figure 1a) can be fully indexed as a brucite-like phase with hexagonal lattice parameters of $a = 0.3153(3)$ nm and $c = 0.4632(1)$ nm. Compared with $\beta$-$Co(OH)_2$, $a$ is slightly smaller, which might be attributed to the different effective ionic radii of $Ni^{2+}$ and $Co^{2+}$ ($Co^{2+}$: 73.5 pm, high-spin; $Ni^{2+}$: 70.0 pm, high-spin).[14] The molar ratio of metal ions in the sample was quantified by chemical analyses as Co:Ni = 2.13:1, indicating that cobalt and nickel ions can be coprecipitated from the solution via

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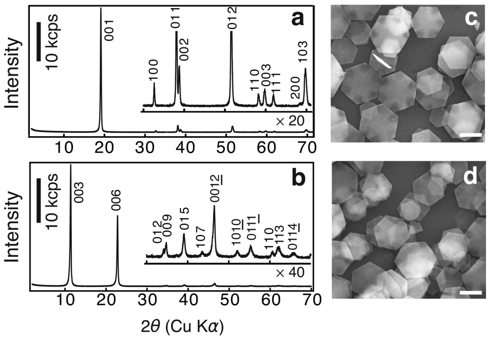

**Figure 1.** XRD patterns and SEM images of the samples: (a, c) Brucite-like $Co_{2/3}-Ni_{1/3}$ hydroxides; (b, d) $Co_{2/3}-Ni_{1/3}-Br$ LDHs. Scale bar is 2 $\mu$m.

HMT hydrolysis. The chemical formula of the sample is thus expressed as $Co_{2/3}Ni_{1/3}(OH)_2$.

After the $Co_{2/3}-Ni_{1/3}$ hydroxides were treated with excessive bromine in acetonitrile for 24 h, the color changed from the initial light-pink to yellow-green, implying that a portion of divalent ions was oxidized into a trivalent state. A typical XRD pattern is shown in Figure 1b. All diffraction peaks can be indexed as a rhombohedral structure with unit cell parameters of $a$ = 0.3093(2) nm and $c$ = 2.325(1) nm. Sharp basal reflections attributable to an interlayer distance of 0.77 nm were observed. The XRD pattern fits well with $Br^-$-intercalated $Co^{2+}{}_{2/3}-Co^{3+}{}_{1/3}$ and Mg−Al LDHs,[8b,15] suggesting the successful insertion of bromide anions between the slabs of brucite-like $Co_{2/3}-Ni_{1/3}$ hydroxides, and the formation of $Co_{2/3}-Ni_{1/3}-Br$ LDHs.

Chemical analyses determined that the molar ratio of divalent ions and trivalent ions in as-prepared $Co_{2/3}-Ni_{1/3}-Br$ LDHs was 2:1, indicating that only 1/3 of divalent ions were oxidized into a trivalent state even though excessive bromine was applied. To gain insight into which element, $Co^{2+}$ or $Ni^{2+}$, in the brucite-like $Co_{2/3}-Ni_{1/3}$ hydroxides is oxidized into a higher oxidation state, we carried out control experiments to clarify the structure of the $Co_{2/3}-Ni_{1/3}-Br$ LDHs. When treating $\beta$-$Ni(OH)_2$ prepared by HMT hydrolysis, the sample was almost unchanged in terms of XRD data and sample color, suggesting that $Ni^{2+}$ confined in the brucite layers could not be transformed into a higher oxidation state under this condition. Combined with our earlier result that $Co^{2+}$ within the brucite layers was partially oxidized into $Co^{3+}$ by bromine,[8b] it is reasonable to deduce that $M^{3+}$ in the $Co_{2/3}-Ni_{1/3}-Br$ LDHs is $Co^{3+}$ whereas $M^{2+}$ is a mixture of $Co^{2+}$ and $Ni^{2+}$. X-ray photoelectron spectra (XPS) further support for this conclusion (see the Supporting Information, Figure S1). On the basis of the chemical analysis results and above discussion, the chemical formula of as-prepared $Co_{2/3}-Ni_{1/3}-Br$ LDHs may be expressed as $[(Co^{2+}{}_{1/3}Ni^{2+}{}_{1/3}Co^{3+}{}_{1/3})(OH^-)_2][Br^-{}_{1/3}\cdot 0.5H_2O]$. Namely, the formation of $Co_{2/3}-Ni_{1/3}-Br$ LDHs from brucite-like $Co_{2/3}-Ni_{1/3}$ hydroxides can be regarded as the partial oxidation of $Co^{2+}$ to $Co^{3+}$ by bromine and the simultaneous intercalation of bromide anions into the galleries, as shown below

$$Co^{2+}{}_{2/3}Ni^{2+}{}_{1/3}(OH^-)_2 + 1/6Br_2 + 0.5H_2O \rightarrow [(Co^{2+}{}_{1/3}Ni^{2+}{}_{1/3}Co^{3+}{}_{1/3})(OH^-)_2][Br^-{}_{1/3}\cdot 0.5H_2O] \tag{1}$$

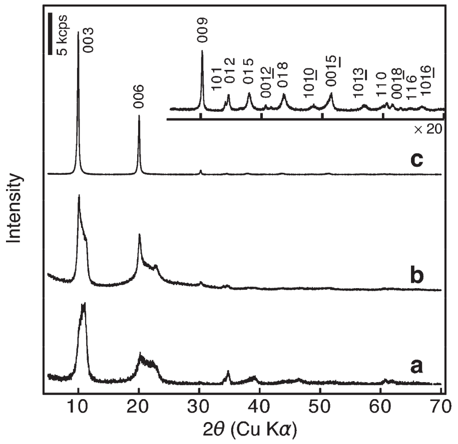

**Figure 2.** XRD patterns of the nitrate intercalated $Co_{2/3}-Ni_{1/3}$ LDH samples prepared via different anion-exchange routes: (a) normal anion-exchange; (b) anion-exchange with the addition of 2 mM acid; (c) anion-exchange in an ethanol/water mixed solution. Inset is an enlargement of the high angular portion of XRD pattern c.

Scanning electron microscope (SEM) observations reveal that the $Co_{2/3}-Ni_{1/3}$ hydroxides consist of hexagonal platelets with lateral size of 1−4 $\mu$m and thickness of several tens of nanometers (Figure 1c). The microplatelets are well-developed with a regular hexagonal frame, sharp corners and smooth surface. After the $Co_{2/3}-Ni_{1/3}$ hydroxides were transformed into an LDH phase, the size and shape remained unchanged (Figure 1d). The morphological preservation supports the topotactic nature of this oxidative intercalation reaction.

To further explore their physicochemical properties, as-prepared $Co_{2/3}-Ni_{1/3}-Br$ LDHs were transformed into other anionic forms through anion exchange. Normal experimental procedures under $N_2$ gas protection could not yield high-quality products. For example, Figure 2a depicts the XRD pattern of a sample obtained by treating $Co_{2/3}-Ni_{1/3}-Br$ powder with 1.5 M $NaNO_3$ solution for 24 h, clearly indicating incomplete exchange. Elemental analysis detected a large amount of carbon in this sample (see the Supporting Information, Table S1). Although the carbon content cannot be quantitatively treated because of possible extrinsic contamination and drifting background in the analysis, severe carbonate contamination for this sample is obvious. The rate of exchange to nitrate form is estimated based on nitrogen content because of its higher reliability. The obtained value was surprisingly low, 15%. In our previous studies of $Co^{2+}{}_{2/3}-Fe^{3+}{}_{1/3}$ and $Co^{2+}{}_{2/3}-Co^{3+}{}_{1/3}$ LDHs, we demonstrated that the addition of diluted acid in the reaction system reduced the carbonate contamination.[8] We thus carried out the anion-exchange experiments on $Co-Ni_{1/3}$ LDHs under acidic conditions (acid concentration: 2 mM).

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The exchange rate increased to about 55%, but the sample quality was still not satisfactory, as apparent from XRD data (Figure 2, pattern b). To fully expel the carbonate contamination, a higher dosage of acid may be required, which would inevitably cause the dissolution of LDH powder because of its low acid tolerance. In this study, we found that the exchange in an ethanol/water mixed solution (1:1 in volume) could produce a highly crystalline sample, as confirmed by the sharp and symmetric *hkl* diffraction peaks in the corresponding XRD pattern (Figure 2, pattern c). Basal spacing of 0.88 nm is close to that of the nitrate intercalated $Al^{3+}$-based LDHs.[7a,b] Lattice parameter refinement confirms a rhombohedral structure with $a = 0.3092(1)$ nm and $c = 2.652(2)$ nm. In the ATR-IR (ATR: attenuated total reflection) spectrum, two peaks centered at 1339 $cm^{-1}$ and 1415 $cm^{-1}$ are observed (see the Supporting Information, Figure S2), which can be assigned to the $\nu_3$ vibration modes of $NO_3^-$ anions. The splitting of the $\nu_3$ vibration modes indicates that the nitrate anions in the galleries retain $C_{2v}$ symmetry with their molecular planes vertically oriented to the host layers.[16] This spectral feature differs from that of the sample obtained in the normal anion-exchange process showing a sharp peak at 1342 $cm^{-1}$ attributable to a vibration mode of $CO_3^{2-}$. The higher exchange rate (about 90%) and the lower carbonate content (carbon content: 0.50% in weight, the same as that of the pristine $Co_{2/3}-Ni_{1/3}-Br$ sample) as well as the XRD and ATR-IR data indicate that the addition of ethanol can effectively minimize carbonate contamination and promote anion exchange. A variety of anions ranging from inorganic to organic species, such as perchlorate ($ClO_4^-$), acetate ($CH_3COO^-$), chloride ($Cl^-$), and dodecyl sulfate ($C_{12}H_{25}OSO_3^-$), can be exchanged into the galleries through this ethanol-assisted approach, demonstrating its wide applicability. The XRD patterns shown in Figure 3 clearly indicate that the products are of high quality.

The role of ethanol may be associated with its solvent effect on multiple equilibria including the dissolution of $CO_2$, the formation of carbonate acid and its ionization into the carbonate ions, and so on. As ethanol is an adverse solvent for carbonate salts, carbonate species have lower solubility in the ethanol/water binary solution than in water. This may account for the low carbonate contamination in the samples prepared by the ethanol-assisted approach. In addition, ethanol is a noncorrosive reagent; the weight loss of the acid-sensitive LDH crystals in such a neutral solution is negligible. The mild anion-exchange process proceeding in such binary solution is also favorable for maintaining the high sample quality.

Previously, a series of $Al^{3+}$-based LDHs was successfully exfoliated into unilamellar nanosheets on contact with formamide; the best result was achieved for the $NO_3^-$ intercalated form.[6,7] In concurrence with the $Al^{3+}$-based LDHs, the $NO_3^-$ intercalated $Co_{2/3}-Ni_{1/3}$ LDHs can be readily exfoliated in formamide. A translucent colloidal suspension with a yellow-green color was attained after the solid powder was dispersed in formamide and shaken for 24 h. Clear Tyndall light scattering was observed when the suspension was side irradiated with a light beam. Gluelike aggregates were recovered from the colloidal suspension after a high-speed centrifugation (30 000 rpm). The corresponding XRD pattern did not show the basal peaks (Figure 4a), but there was a noticeably high background in the low angular region (below 10°), which can be taken as evidence for total delamination.[7a,b,17] A tapping-mode atomic force microscopy (AFM) image (Figure 4b) displays two-dimensional ultrathin nanosheets with lateral dimensions of several hundred nanometers. These ultrathin nanosheets are irregular in shape, which is due to breakage or fracture during the delamination process. The average thickness of the nanosheets is about 0.80 ± 0.02 nm, which is close to that observed for LDH nanosheets reported to date.[7,8] Such a thickness may be explained as the sum of crystallographic thickness of the LDH layer, adsorbed $NO_3^-$ anions and formamide molecules,[7a] supporting the formation of macromolecular $Co_{2/3}-Ni_{1/3}$ hydroxide nanosheets bearing a positive charge.

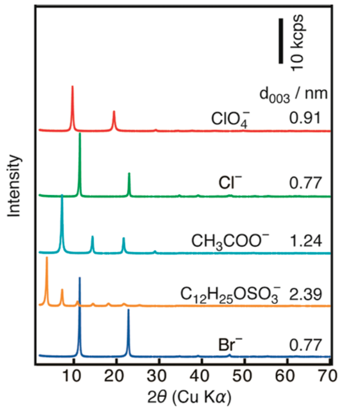

**Figure 3.** XRD patterns of $Co_{2/3}-Ni_{1/3}$ LDHs intercalated with various anions (dodecyl sulfate, acetate, chloride, and perchlorate) in comparison with the pristine $Co_{2/3}-Ni_{1/3}-Br$ LDH sample.

**Composition-Tuned Synthesis of Co–Ni LDHs and Their Exfoliation.** Brucite-like Co–Ni hydroxides with a tunable Co/Ni ratio (abbreviated as $Co_{1-x}Ni_x(OH)_2$, $0 \leq x \leq 1$) could be prepared by the HMT hydrolysis method (see the Supporting Information, Figures S3–S5). Chemical analyses found that the Co/Ni ratio in the powder was consistent with that in the starting solution. Among as-synthesized $Co_{1-x}Ni_x(OH)_2$, high-quality samples

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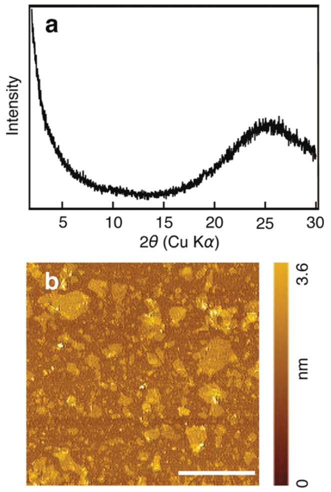

**Figure 4.** (a) XRD pattern of the gel-like aggregates centrifuged from the suspension. The halo at 20−30° is due to formamide. (b) AFM image of the $Co_{2/3}-Ni_{1/3}$ hydroxide nanosheets. The scale bar is 1 $\mu$m.

were yielded for the cobalt-rich side ($x \leq 0.5$), as revealed by the sharp, intense basal diffraction peaks in the XRD patterns; the basal peaks gradually broadened for the nickel-rich ones ($x > 0.5$). Lattice constant refinement indicates that both parameters $a$ and $c$ decrease linearly with increasing nickel content, following the Vegard's correlation. SEM images show that the cobalt-rich samples were composed of well-developed hexagonal microplatelets with sharp corners, similar to $\beta$-$Co(OH)_2$ prepared by HMT hydrolysis. For the nickel-rich ones, the microplatelets were less-developed with smaller average size as well as round corners, and $\beta$-$Ni(OH)_2$ was mostly irregular aggregates of thin flakes. After the brucite-like samples of $Co_{1-x}Ni_x(OH)_2$ were subjected to oxidation with bromine, pure-phase Co−Ni LDHs (abbreviated as $Co_{1-x}-Ni_x$ LDHs, $0\leq x \leq 1$) were attained for the cobalt-rich samples, as evidenced from the XRD patterns displayed in Figure 5a. In contrast, there was always a residual brucite-like phase in the nickel-rich samples. For the pure-phase $Co_{1-x}-Ni_x-Br$ LDHs, in-plane parameter $a$ decreases linearly with increasing nickel content (Figure 5b), whereas parameter $c$ is nearly invariable. Importantly, the molar ratio of divalent ions to trivalent ions in the $Co_{1-x}-Ni_x-Br$ LDHs given by chemical analyses was unexceptional at 2:1, which is the same as the $Co_{2/3}-Ni_{1/3}-Br$ LDHs. The oxidative intercalation reaction is thus generally expressed as

$$Co^{2+}{}_{1-x}Ni^{2+}{}_{x}(OH^{-})_2 + 1/6Br_2 + 0.5H_2O \rightarrow [(Co^{2+}{}_{1-3x/2}Ni^{2+}{}_{3x/2})_{2/3}Co^{3+}{}_{1/3}(OH^{-})_2][Br^{-}{}_{1/3}\cdot 0.5H_2O]\ (0\leq x\leq 0.5) \tag{2}$$

Equation 2 indicates that the $Co_{1-x}-Ni_x-Br$ LDHs synthesized through the oxidative intercalation reaction have the same valence structure although the nickel content varies over wide range. A similar tendency was reported in the aerial oxidation of brucite-like $Fe(OH)_2$ to hydrotalcite-like green rust with $Fe^{2+}/Fe^{3+}$ at 2:1 or 3:1 depending on the anions.[18] These results provide some insight into the oxidative intercalation reaction. The $M^{2+}/M^{3+}$ ratio or the host layer charge should be determined by the interplay between the host layers and guests (here, the guests represent the bromide anions produced in situ in the oxidative intercalation process). For an LDH compound $[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH^{-})_2]^{x+}[(A^{n-}{}_{x/n})^{x-}\cdot mH_2O]$ ($1/5 \leq x \leq 1/3$), the charge of host layer is proportional to $x$, i.e., the amount of $M^{3+}$ ions. In the oxidative intercalation reaction, a higher layer charge, produced by oxidizing more $M^{2+}$ into $M^{3+}$, is beneficial for stabilizing the LDH structure by strengthening the electrostatic interaction between host layers and guests. Nevertheless, in the galleries, the guest-to-guest repulsion makes a negative contribution to the stabilization of LDH structure, especially for a structure with higher charge density or higher population of anions. Accordingly, $Co_{1-x}-Ni_x-Br$ LDHs presenting a preferential $M^{2+}/M^{3+}$ ratio of 2:1 suggest that this interplay reaches a balance as 1/3 of the $M^{2+}$ is transformed into $M^{3+}$. Several studies indicate that in the LDH compound with $M^{2+}/M^{3+}$ ratio of 2:1, the $M^{3+}$ ions are neatly arranged in a trigonal supercell,[8b,19] which favors the formation of a stable LDH structure by avoiding direct neighboring of trivalent ions. In the topochemical process, bromide anions were incorporated into vacant interlayer sites of the brucite-like hydroxides to fulfill the formation of LDH structure (see the Supporting Information, Figure S7). In the case of $Co_{2/3}-Ni_{1/3}-Br$ LDHs, considering that

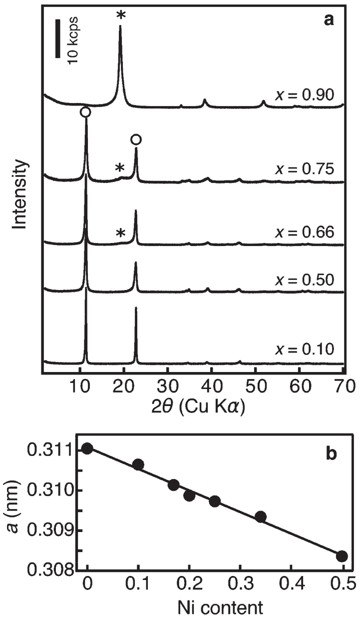

**Figure 5.** (a) XRD patterns of the samples produced by treating brucite-like $Co_{1-x}-Ni_x$ hydroxides with bromine. The diffraction peaks marked with an asterisk and circle correspond to brucite-like $Co_{1-x}-Ni_x$ hydroxides and LDH phase, respectively; (b) variation of in-plane parameter $a$ of $Co_{1-x}-Ni_x-Br$ LDHs as a function of Ni content.

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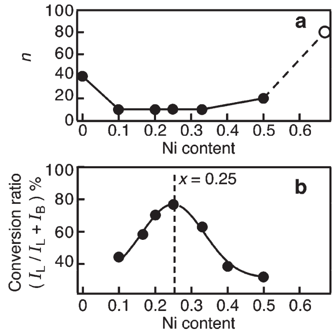

**Figure 6.** (a) Plot of $n$ vs nickel content. The dashed line and open circle indicate that pure-phase LDHs could not be attained even when a large amount of bromine was applied; (b) plot of the conversion ratio of the oxidative intercalation reaction vs nickel content. The conversion ratio is calculated by counting the first basal peak intensity ratio of the brucite-like hydroxides ($I_B$) and LDH phase ($I_L$) in treating the brucite-like $Co_{1-x}-Ni_x$ hydroxides with stoichiometric bromine.

the ionic diameter of $Br^-$ (0.392 nm) is much larger than the $OH^- - OH^-$ distance (equal to parameter $a$, 0.309 nm), if a vacant site is occupied by one $Br^-$, the first-nearest neighboring site cannot be occupied by another $Br^-$. This restriction would lead to an ordered array of $Br^-$ separated by distance $a\sqrt{3}$ and each $Br^-$ would be associated with two $M^{2+}$ and one $M^{3+}$, giving a $M^{2+}/M^{3+}$ ratio of 2:1 (see the Supporting Information, Figure S8). This anion ordering has been observed in the sulfate-intercalated green rust with $Fe^{2+}/Fe^{3+}$ ratio of 2:1.[18b] Therefore, the $Co_{1-x}-Ni_x-Br$ LDHs with a $M^{2+}/M^{3+}$ ratio of 2:1 may represent the most thermodynamically favorable form among those allowing valence structure with $1/5 \leq x \leq 1/3$.

Equation 2 means that oxidizing 1 mol of brucite-like $Co_{1-x}-Ni_x$ hydroxides to LDHs containing 1/3 $Co^{3+}$ nominally requires 1/6 mol of $Br_2$. In practice, an excessive amount of bromine is needed to produce a pure phase of $Co_{1-x}-Ni_x-Br$ LDHs. We define $n$ as the multiple of bromine amount practically applied to that theoretically required. Figure 6a presents $n$ versus nickel content (treatment period: 24 h). Note that less bromine is required to completely transform the brucite-like $Co_{1-x}-Ni_x$ hydroxides into the corresponding LDH phase compared to that in $\beta$-$Co(OH)_2$ ($n$ = 40; treatment period, 7 days), suggesting that the brucite-like $Co_{1-x}-Ni_x$ hydroxides are more prone to transformation into the LDH structure in the oxidative intercalation reaction. In a control experiment, a sample was made by mechanically mixing brucite-like $Co(OH)_2$ and $Ni(OH)_2$ at a molar ratio of 2:1. After the sample was treated with bromine under the same condition as the formation of $Co^{2+}{}_{2/3}-Co^{3+}{}_{1/3}$ LDHs, XRD data showed that the product was a mixture of LDH and brucite-like phase, which obviously differs from the formation of $Co_{2/3}-Ni_{1/3}-Br$ LDHs. Thus, the nickel ions and cobalt ions cosubstituted in the brucite layers produce some cooperative activities. Moreover, in another control experiment, brucite-like $Co_{1-x}-Ni_x$ hydroxides (2 mmol) were treated with stoichiometric bromine (1/3 mmol) for 24 h. The conversion ratio of the reaction was estimated from XRD data by counting the first basal peak intensity of the brucite-like hydroxides ($I_B$) and the LDH phase ($I_L$).

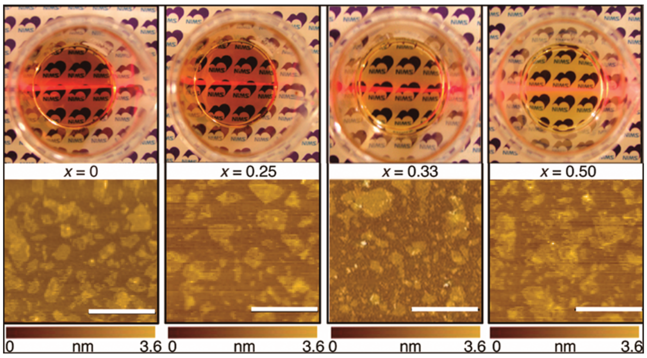

**Figure 7.** Photographs of nanosheet suspensions of the $Co_{1-x}-Ni_x$ LDHs ($x$ = 0, 0.25, 0.33, and 0.50) and AFM images of the nanosheets. The scale bar in the AFM images is 1 $\mu$m.

The plot of the conversion ratio against nickel content produces a bell-shaped curve (Figure 6b), showing that the conversion ratio varies nonmonotonically according to the amount of cobalt ions. Instead, a maximum value is observed for the samples with $x$ value around 0.25. This qualitative analysis implies that substituting a portion of cobalt ions with nickel ions in the brucite layers could promote the formation of LDHs, even though the nickel ions are inert to the oxidation of bromine. Similar phenomena were observed in the case of layered $Fe^{2+}-Fe^{3+}$ hydroxides (green rust), which were more reactive in reducing $AsO_2$ in solution than $Fe(OH)_2$.[20] Calculations suggested that the $Fe^{2+}-Fe^{3+}$ valence interchange within the host layers might have accounted for its higher activities. For brucite-like $Co_{1-x}-Ni_x$ hydroxides, the nickel ions may have been involved in the charge-hopping process during the oxidative intercalation reaction. Because the charge-hopping process is largely influenced by the metal ion distribution,[21] the behavior of $Co_{1-x}-Ni_x$ hydroxides in the oxidative intercalation reaction would be determined by both the Co/Ni ratio and the ion distribution in the host layers.

After transforming the as-prepared $Co_{1-x}-Ni_x-Br$ LDHs into the corresponding $NO_3^-$ intercalated form through the ethanol-assisted anion-exchange approach, $Co_{1-x}-Ni_x$ LDHs with tunable Co/Ni ratio could be completely exfoliated into ultrathin nanosheets in formamide. The colloidal suspensions exhibited different colors as their components varied (see Figure 7). The UV−vis spectra of the colloidal suspensions are shown in Figure 8. A broad band ranging from 370 to 520 nm was observed for the $Co^{2+}-Co^{3+}$ hydroxide nanosheet suspension, which results from the ${}^4A_{1g}(F)-{}^4T_{1g}(P)$ of $Co^{2+}$ in an octahedral coordination.[22] For the $Co_{1-x}-Ni_x$ LDH samples, absorbance in the range from 370 to 520 nm gradually decreased with decreasing $Co^{2+}$ content. The color change observed in the photograph should be related to the different amount of $Co^{2+}$ confined within the nanosheets.

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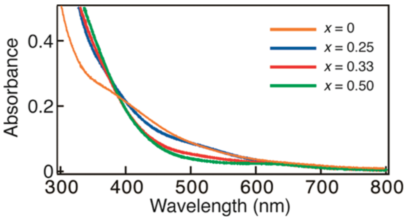

**Figure 8.** UV−vis spectra of nanosheet suspensions of the $Co_{1-x}-Ni_x$ LDHs.

## Conclusions

We successfully synthesized highly crystallized Co−Ni LDHs with tunable composition via the topochemical oxidative intercalation reaction. The Co−Ni LDH compounds, derived from brucite-like Co−Ni hydroxides, can be generally expressed in a formula as $[(Co^{2+}{}_{1-3x/2}Ni^{2+}{}_{3x/2})_{2/3}Co^{3+}{}_{1/3}](OH^-)_2[Br^-{}_{1/3}\cdot 0.5H_2O]$ $(0 \le x \le 0.5)$ characterized by $M^{2+}/M^{3+}$ ratio of 2:1. We examined the factors influencing the topochemical reaction and clarified that brucite-like Co−Ni hydroxides were more prone to transformation into the corresponding LDH phase compared with $\beta$-$Co(OH)_2$ under the same conditions. These results provide insight into the mechanism of the oxidative intercalation reaction and are beneficial for understanding the physicochemical properties of this class of layered Co−Ni hydroxides. An ethanol-assisted procedure was effective for converting the bromide intercalated Co−Ni LDHs into various inorganic or organic anionic forms with substantially suppressed carbonate contamination. This method may be extended to diverse mixed-solvent systems other than ethanol/water and shows promise for achieving high-quality LDH samples. The Co−Ni−$NO_3$ LDHs were successfully exfoliated into unilamellar nanosheets in formamide. The Co−Ni hydroxide nanosheets with tunable Co/Ni ratio may be useful in exploring new magneto-optical or electrochemical devices.

## Experimental Section

**Synthesis of Brucite-like $Co_{1-x}-Ni_x$ Hydroxides.** The synthesis of brucite-like $Co_{1-x}-Ni_x$ hydroxides is described by taking $Co_{2/3}-Ni_{1/3}$ hydroxides as an example. Typically, 5 mmol of cobalt chloride ($CoCl_2\cdot 6H_2O$), 2.5 mmol of nickel chloride ($NiCl_2\cdot 6H_2O$) and 45 mmol of HMT were dissolved in 1000 $cm^3$ of deionized water. The $CoCl_2-NiCl_2$−HMT solution was refluxed for 5 h under continuous magnetic stirring and nitrogen protection. The light-pink precipitate was recovered by filtration, washed with deionized water and anhydrous ethanol in turn, and finally air-dried at room temperature. To synthesize brucite-like $Co_{1-x}-Ni_x$ hydroxides with variable Co/Ni ratio, we dissolved $CoCl_2\cdot 6H_2O$ and $NiCl_2\cdot 6H_2O$ with the desired molar ratio in water at a total concentration of 7.5 mM. The following procedures were the same as that in the synthesis of $Co_{2/3}-Ni_{1/3}$ hydroxides.

**Topochemical Oxidation to Synthesize $Co_{1-x}-Ni_x$−Br LDHs.** $Co_{1-x}-Ni_x$−Br LDHs were prepared by treating brucite-type $Co_{1-x}-Ni_x$ hydroxides with excessive bromine in acetonitrile. For example, to prepare $Co_{2/3}-Ni_{1/3}$−Br LDHs, 2 mmol (0.186 g) of as-synthesized brucite-like $Co_{2/3}-Ni_{1/3}$ hydroxides were dispersed in 100 $cm^3$ of acetonitrile containing 6.67 mmol of bromine. The mixture was sealed in an airtight capped flask and magnetically stirred for 24 h to promote complete transformation. The yellow-green product, identified as bromide intercalated $Co_{1-x}-Ni_x$ LDHs, was collected by centrifugation and washed with copious amounts of anhydrous ethanol to remove the excess bromine adsorbed on the powder. The synthetic procedures for $Co_{1-x}-Ni_x$ LDHs with variable Co/Ni ratios were identical except for the amount of bromine applied.

**Anion Exchange and Exfoliation of the $Co_{1-x}-Ni_x$ LDHs.** $Co_{1-x}-Ni_x$ LDHs intercalated with various anions were prepared via an ethanol-assisted anion-exchange approach to minimize the carbonate contamination. For instance, to prepare the nitrate intercalated $Co_{2/3}-Ni_{1/3}$ LDHs, a nitrate solution (1.5 M) was prepared by dissolving 0.3 mol of $NaNO_3$ into 200 $cm^3$ of ethanol/water binary liquid (1:1 v/v) in a flask. 0.25 g of $Co_{2/3}-Ni_{1/3}$−Br LDH powder was dispersed into the solution after purging with nitrogen gas. The vessel was tightly capped and mechanically shaken for 24 h at room temperature. The product was filtered, washed with anhydrous ethanol, and air-dried for further characterization.

To prepare $Co_{1-x}-Ni_x$ hydroxide nanosheets, we dispersed 0.05 g of $NO_3^-$-intercalated $Co_{1-x}-Ni_x$ LDH powder in 100 $cm^3$ of formamide in a flask. After purging with nitrogen gas and capping tightly, the flask was agitated in a mechanical shaker at a speed of 170 rpm for 24 h. The resultant translucent suspension was further treated by centrifugation at 2000 rpm for 10 min to remove possible unexfoliated particles.

**Sample Characterization.** A Rigaku Rint-2000 diffractometer with monochromatic Cu Kα radiation ($\lambda$ = 0.15405 nm) was employed to examine the phase and purity of the samples. The morphology and size of the products were examined with a Keyence VE8800 SEM. A Seiko SPA 400 atomic force microscopy system was used to examine the topography of the nanosheets. AFM images were acquired in tapping-mode using a Si-tip cantilever with a force constant of 20 N $m^{-1}$. ATR-IR spectra were measured on a Perkin-Elmer Spectrometer with an ATR accessory (Perkin-Elmer L1200361 single reflection-type with diamond/ZnSe top-plate). UV−vis absorption spectra were recorded using a Hitachi U-4100 spectrophotometer. X-ray photoelectron spectra were recorded on a Physical Electronics XPS-5700 spectrometer equipped with Al Kα X-ray line (1486.6 eV).

The Co/Ni ratio in the $Co_{1-x}-Ni_x$ hydroxides was determined by a chemical titration method similar to that used for $Co_{1-x}-Ni_x$ alloy.[23] Typically, a weighed amount of $Co_{1-x}-Ni_x$ hydroxide powder (about 0.02 g) was dissolved in diluted HCl and separated into two equal aliquots. One was directly titrated with EDTA using murexide as an indicator. This gave the total amount of divalent ions in the sample. To determine the nickel content, we added 1.0 g of $(NH_4)_2S_2O_8$ and 0.5 g of NaF as well as excessive ammonia to the solution. This mixture was refluxed to oxidize the $Co^{2+}$ ions into $Co^{3+}$ with the simultaneous formation of an ammonia complex. The amount of nickel ions was then determined by EDTA titration. The content of cobalt ions was calculated based on the titration results. The amount of $Co^{3+}$ in the $Co_{1-x}-Ni_x$−Br LDHs was determined by a procedure similar to the analysis of monometallic $Co^{2+}-Co^{3+}$ LDHs.[8b] The LDH powder was dissolved in a solution of

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$H_2SO_4$ and excessive iodide. The stoichiometric amount of iodine produced from the oxidation of $I^-$ by $Co^{3+}$ in acidic solution was back-titrated with $Na_2S_2O_3$.

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**Supporting Information Available:** XPS spectra of the brucite-like $Co_{2/3}-Ni_{1/3}$ hydroxides and corresponding LDHs, Elemental content (N,C,H), ATR-IR spectra of the $Co_{2/3}-Ni_{1/3}-Br$ LDHs and the nitrate samples prepared via the normal anion-exchange method, with the addition of acid and the ethanol-assisted method, XRD patterns, SEM images and lattice parameters of the brucite-like $Co_{1-x}-Ni_x$ hydroxides, XRD patterns of the $Co_{1-x}-Ni_x-Br$ and $Co_{1-x}-Ni_x-NO_3$ LDHs, illustrations of the stacking sequence of the LDH phase and brucite phase, XRD patterns of the samples by treating the brucite-like $Co_{1-x}-Ni_x$ hydroxides with different amounts of bromine, and XRD pattern of the product after treating a mixture of $\beta$-Co(OH)$_2$ and $\beta$-Ni(OH)$_2$ at a molar ratio of 2:1 with 40 times the amount of bromine (PDF). This information is available free of charge via the Internet at the http://pubs.acs.org.