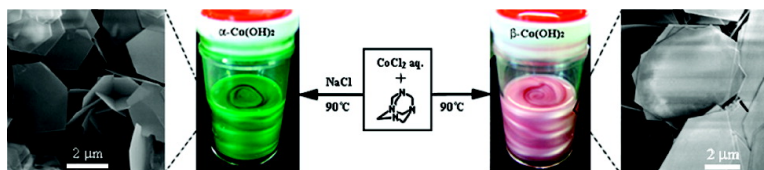Article

# Selective and Controlled Synthesis of ☐- and β-Cobalt Hydroxides in Highly Developed Hexagonal Platelets

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# Selective and Controlled Synthesis of α- and β-Cobalt Hydroxides in Highly Developed Hexagonal Platelets

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**Abstract:** We report on the controlled synthesis of single-crystal platelets of α- and β-Co(OH)$_2$ via homogeneous precipitation using hexamethylenetetramine as a hydrolysis agent. The α- and β-Co(OH)$_2$ hexagonal platelets of several micrometers in width and about 15 nm in thickness were reproducibly yielded in rather dilute CoCl$_2$ solutions in the presence and absence of NaCl at 90 °C, respectively. The phase and size control of the products were achieved by varying both CoCl$_2$ and NaCl concentrations. Polarized optical microscope observations revealed clear liquid crystallinity of colloidal suspensions of these high aspect-ratio platelets. The as-prepared α-Co(OH)$_2$ containing interlayer chloride ions was intercalated with various inorganic or organic anions, keeping its high crystallinity and hexagonal platelike morphology.

## Introduction

Hydroxides of cobalt are well-known to crystallize in two polymorphs, α and β.[1] The β-form is a stoichiometric phase of the composition Co(OH)$_2$ with brucite-like structure and consists of a hexagonal packing of hydroxyl ions with Co(II) occupying alternate rows of octahedral sites,[2] while the α-hydroxides are reported to be isostructural with hydrotalcite-like compounds that consist of positively charged Co(OH)$_{2-x}$ layers and charge balancing anions (e.g., NO$_3^-$, CO$_3^{2-}$, Cl$^-$, etc.) in the interlayer gallery.[1a,3] The α-hydroxides thus have a larger interlayer spacing (usually >7 Å, dependent on intercalated anions) than that of the β-form (4.6 Å). Cobalt hydroxides have recently received increasing attention due to their many important technological applications. For example, β-Co(OH)$_2$ has been used as additives of alkaline secondary batteries and as precursors of heterogeneous catalysts.[4] β-Co(OH)$_2$/zeolite nanocomposite has been found to have a very high specific capacitance and shows a potential application as an electro-

chemical supercapacitor.[5] A further very interesting application of β-Co(OH)$_2$ is as reactive templates (precursors) for highly textured thermoelectric cobaltite ceramics such as NaCo$_2$O$_4$ and Ca$_x$CoO$_2$, because its hexagonal layered structure has lattice matching with cobaltite materials.[6] On the other hand, α-phase compounds are theoretically expected to exhibit superior electrochemical activity as compared to the β-form.[1b] In this respect, the α-hydroxides may be more promising electrode materials. Furthermore, the α-hydroxides intercalated organic anions show long-range magnetic ordering and are regarded as new candidates for organic magnetic materials.[7]

The synthesis of single-crystal β-Co(OH)$_2$ hexagonal platelets is relatively easily achieved and has been much demonstrated.[8] Nevertheless, the platelets prepared usually have lateral sizes of submicrometers and small width-to-thickness ratios (aspect ratios) of around 10. In fact, large platelets of β-Co(OH)$_2$ with a narrow particle size distribution and a large aspect ratio are more desirable for the applications and the evaluations of their physicochemical properties. For example, uniformly sized and high aspect-ratio platelets of β-Co(OH)$_2$ are optimum templates for the synthesis of highly textured cobaltite ceramics because the reactive templated grain growth (RTGG) process requires good alignment of template particles.[6] In addition, such high-quality platelets are also expected to show interesting liquid crystalline behaviors as have been extensively documented for

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various mineral platelets.[9] As compared to $\beta$-Co(OH)$_2$, single-crystal particles of $\alpha$-hydroxides are difficult to synthesize because the $\alpha$-phase is metastable and transforms rapidly to the $\beta$-form during synthesis or upon storage in strong alkaline media.[8c] Many attempts have been made to prepare the $\alpha$-hydroxides by electrochemical and chemical syntheses including urea and ammonia precipitation as well as sonication-assisted NaOH precipitation methods.[3] However, all of the $\alpha$-hydroxides synthesized so far were poorly crystalline and had a turbostratically disordered structure, in which the layers were randomly oriented about the *c*-axis, and they usually occurred as aggregates of thin tangled films without any particular morphology. The synthesis of single-crystal $\alpha$-hydroxides with a well-defined morphology is still a major challenge and is also of technological importance, because it should lead to new types of applications or enhanced performances.

Although many efforts have been made on the synthesis of cobalt hydroxides, the control of their phase, morphology, size, and crystallinity has not been fully established yet. In this study, uniform and single-crystal hexagonal platelets of $\alpha$- and $\beta$-Co(OH)$_2$ were synthesized controllably by homogeneous precipitation from a much dilute cobalt chloride solution using hexamethylenetetramine (HMT) as a hydrolysis agent. The morphology, size, composition, structure, and liquid crystallinity of the platelets were examined in detail. Well-crystallized hexagonal platelets of $\alpha$-cobalt hydroxides intercalated with various inorganic and organic anions were further prepared from the as-prepared $\alpha$-cobalt hydroxide platelets in chloride form via a simple anion-exchange process.

## Experimental Section

**Synthesis of $\alpha$-Co(OH)$_2$.** The synthesis was performed in a beaker under an ambient atmosphere. In a typical procedure, CoCl$_2$·6H$_2$O, NaCl, and HMT were dissolved in 200 cm$^3$ of a 9:1 mixture of deionized water and ethanol to give the final concentrations of 10, 50, and 60 mM, respectively. The reaction solution was then heated at about 90 °C under magnetic stirring. After being heated for about 1 h, a suspension containing green particles resulted. The solid product was filtered and washed with deionized water and anhydrous ethanol several times, and finally air-dried at room temperature.

**Synthesis of $\beta$-Co(OH)$_2$.** The synthetic procedure was similar to the above except that the concentration of CoCl$_2$ was decreased to 5 mM and no NaCl was added. In this case, the resulting product was pink-colored.

**Anion-Exchange Reactions of $\alpha$-Co(OH)$_2$.** The $\alpha$-Co(OH)$_2$ sample in Cl$^-$ form (0.5 g) was dispersed into 250 cm$^3$ of an aqueous solution of 1 M NaNO$_3$ or 0.25 M sodium dodecyl sulfate (SDS, C$_{12}$H$_{25}$OSO$_3$Na). The resulting suspension was heated at 90 °C under stirring and N$_2$ flow. The reaction time was 12 and 48 h for NaNO$_3$ and SDS, respectively. The exchanged products were isolated using the same procedure described for the pristine material.

**Chemical Analysis.** For the $\alpha$-Co(OH)$_2$ sample, its Co content was determined by a complexation titration method. A weighed amount (approximately 25 mg) of sample was dissolved in 5 cm$^3$ of 0.1 M HCl solution. The solution was then further diluted to about 100 cm$^3$ with deionized water, and the pH value was adjusted to about 8.0 with dilute aqueous ammonia. The resulting solution was titrated with a
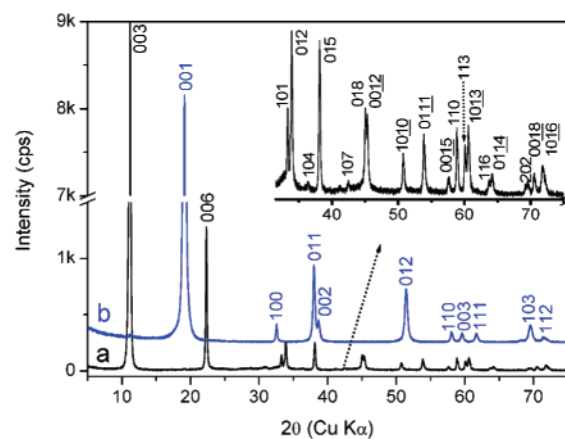
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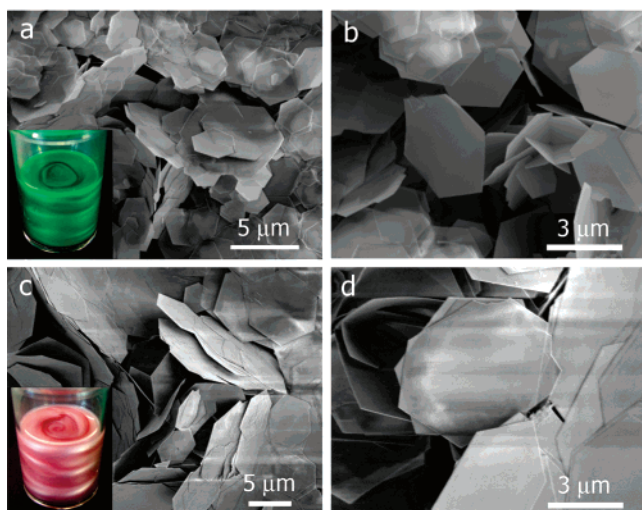
**Figure 1.** XRD patterns of (a) $\alpha$- and (b) $\beta$-Co(OH)$_2$. The inset is an enlarged view of pattern a in high angles.

standard EDTA solution (0.01 M) using murexide as an indicator. The end point was reached when the color of the solution changed from yellow to violet. Note that during the titration process, the pH value of the solution should be maintained in the range of 8.0−8.2 by continuously adding dilute aqueous ammonia. The carbon content was measured via a LECO RC-412 analyzer. The total content of OH$^-$ and CO$_3^{2-}$ ions was determined according to the methods described in the literature.[5d] Typically, approximately 0.2 g of sample was dissolved in an excess of standard acid solution (0.1 M HCl), and the excess acid was back-titrated with a standard base (0.05 M of NaOH) using a pH meter. The Cl$^-$ content was gravimetrically estimated as AgCl after dissolving 0.2 g of sample in diluted HNO$_3$ solution. The unaccounted weight was assigned to the water content to arrive at an approximate formula that was further verified by thermogravimetric analysis (TGA).

**Sample Characterization.** X-ray diffraction (XRD) data were recorded by a Rigaku Rint-2000 diffractometer equipped with a graphite monochromatized Cu K$\alpha$ radiation ($\lambda = 1.5405$ Å). Fourier transform infrared (FT-IR) spectra were measured on a FTS-45RD Bio-Rad infrared spectrophotometer using the KBr pellet technique in the range of 400−4000 cm$^{-1}$. Thermogravimetric analysis (TGA) was carried out using a Rigaku TGA-8120 instrument in the temperature range of 25−800 °C at a heating rate of 1 °C min$^{-1}$ under an air flow. The morphology and dimensions of the products were examined with a Hitachi-S4300E/N scanning electron microscope (SEM). Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), selected-area electron diffraction (SAED), and energy dispersed X-ray spectrometry (EDS) characterizations were performed using a JEOL JEM-3000F transmission electron microscopy at an acceleration voltage of 300 kV. The liquid crystalline phases of the suspensions were observed using an Olympus BX-50 polarizing microscope attached with a color CCD camera.

## Results and Discussion

**Controlled Synthesis of $\alpha$- and $\beta$-Cobalt Hydroxide Platelets.** Well-crystallized platelets of $\alpha$- and $\beta$-Co(OH)$_2$ were obtained by the homogeneous precipitation of dilute CoCl$_2$ solutions with HMT in the presence and absence of NaCl, respectively. Figure 1a shows a XRD pattern of the green product that was prepared in the CoCl$_2$−NaCl−HMT system. The two prominent low-angle reflections at 7.95 and 3.98 Å may be assigned to 003 and 006 reflections of the hydrotalcite-like phase (unit cell with three slabs). Taking into consideration its green color, therefore, this product can be rationally identified as $\alpha$-Co(OH)$_2$. In addition, as can be seen from the magnified XRD pattern (the inset of Figure 1), the *hkl* reflections were

**Figure 2.** Low- and high-magnification SEM images of (a, b) α- and (c, d) β-Co(OH)₂. The insets in panels a and c show bottles of the suspensions obtained by dispersing the platelets in ethanol.



**Figure 3.** XRD patterns of the samples prepared with 5 mM of CoCl₂ solution at 90 °C for different periods of reaction time: (a) 30, (b) 40, (c) 50, and (d) 60 min. The predominant 00*l* reflections of α- and β-phase are indicated as subscripts α and β, respectively.

not only sharp but also symmetric, distinctly differing from the typical broad "saw-tooth" reflections of the as-reported turbostratic structures of α-Co(OH)₂.[3] This feature strongly suggests that the produced material was well crystallized with a regular interlayer registry. The lattice parameters of the as-prepared α-Co(OH)₂ were refined to be $a = 3.1404(8)$ Å and $c = 24.005(8)$ Å. The indices ($-h + k + l = 3n$) clearly indicate a rhombohedral symmetry. Figure 1b shows the XRD pattern of the pink product prepared without NaCl. All diffraction peaks in this pattern can be indexed as the hexagonal cell of brucite-like β-Co(OH)₂ with lattice constants $a = 3.182(1)$ Å and $c = 4.658(2)$ Å (space group $P\bar{3}m1$), which are consistent with the values in the literature (JCPDS card, No. 74-1057). Again, the sharp reflections suggest the highly crystalline nature for the β-Co(OH)₂ product. The high crystallinity of both products can be attributed to the homogeneous precipitation process utilizing HMT hydrolysis, which results in a rather slow rate of nucleation. Typical SEM images shown in Figure 2 reveal that the samples of α- and β-Co(OH)₂ both display an almost perfect hexagonal platelike morphology and that these platelets are rather thin and uniform with widths in the ranges of 2−3 and 5−7 μm, respectively. The thicknesses of both kinds of platelets are estimated to be ∼15 nm. Apparently, the aspect ratios of both kinds of platelets are notably large (>100); especially for the β-Co(OH)₂ platelets, the mean aspect ratio (∼400) is much larger than those (∼10) reported previously.[8] The above results demonstrate that single-crystal particles of α- and β-Co(OH)₂ with a highly developed hexagonal morphology, uniform size, and high aspect ratio can be selectively produced in large scale using the present synthetic scheme.

During the synthesis of β-Co(OH)₂ platelets, the suspension color was green in the initial time (30 min) and sequentially changed to gray and finally (60 min) to pink, implying a spontaneous transformation from initial metastable α-Co(OH)₂ to the thermodynamically stable β-phase. The XRD patterns in Figure 3 demonstrate the proportion of β-phase in samples increased with the time, confirming α → β transformation. Previous studies have revealed that such a transformation proceeded through dissolution of α-Co(OH)₂ particles and subsequent growth of the β-Co(OH)₂ nucleus. This transforma-
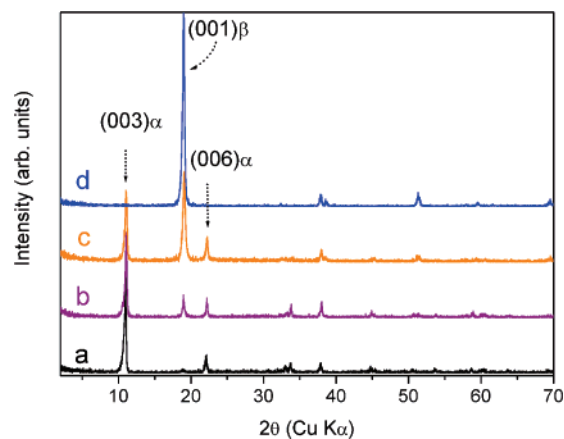
tion could be delayed or even prevented by adding an excess of salts (anions) into the reaction solution.[3f,l,8c] Our experimental results also showed that the addition of a certain amount of NaCl in dilute CoCl₂ solutions could guarantee the yield of pure-phase α-Co(OH)₂ product. In general, the minimal amount of NaCl required was dependent on the CoCl₂ concentration. At a lower concentration of CoCl₂ solution, a lager amount of NaCl was required. At a CoCl₂ concentration of over 25 mM, pure α-phase could be obtained without NaCl for a given time (60 min). When the CoCl₂ concentration was decreased to 20, 15, and 10 mM, pure α-Co(OH)₂ platelets were produced only by adding NaCl with a concentration of at least 20, 35, and 50 mM, respectively. At a CoCl₂ concentration as low as 5 mM, α-Co(OH)₂ platelets were the main product, provided that the NaCl concentration reached 0.1 M. Nevertheless, it should be noted that the extravagant addition of NaCl would result in the formation of large agglomerates (tens of micrometers) of very thick and nonuniform platelets (see Supporting Information, Figure S1). On the other hand, the CoCl₂ concentration was found to have a significant effect on the particle sizes, as illustrated by the SEM images shown in Figure 4. A reaction solution with an increased CoCl₂ concentration (20 mM) yielded platelets with a width of about 2 μm and a thickness of 25 nm (Figure 4a and b). When the concentration was increased to 25 mM, the width of the platelets decreased to 1 μm, but their thickness increased to about 40 nm (Figure 4c and d). Further increasing the concentration to 50 mM resulted in irregular and nonuniform platelets with a width of several hundred nanometers and a thickness of up to 70 nm (Figure 4e and f). It can be concluded that a lower CoCl₂ concentration was favorable for the growth of platelets with larger sizes and higher aspect ratios. The increase in the particle size is possibly due to the decreased number of nucleus originated from the low CoCl₂ concentration.

**Composition and Crystallinity Analyses.** Based on the results of chemical analysis and thermogravimetric measurement, the composition of the as-prepared α-Co(OH)₂ sample was estimated to be $Co(OH)_{1.70}(CO_3)_{0.02}Cl_{0.26} \cdot 0.56H_2O$ (Anal. Calcd: Co, 54.40%; C, 0.22%; OH⁻, 26.68%; Cl⁻, 8.51%. Found: Co, 53.97%; C, 0.20%; OH⁻, 26.59%; Cl⁻, 8.31%). Apparently, the predominant anionic species in the interlayer of the α-Co(OH)₂ sample were Cl⁻ ions, which were accommodated in the interlayer space together with water molecules
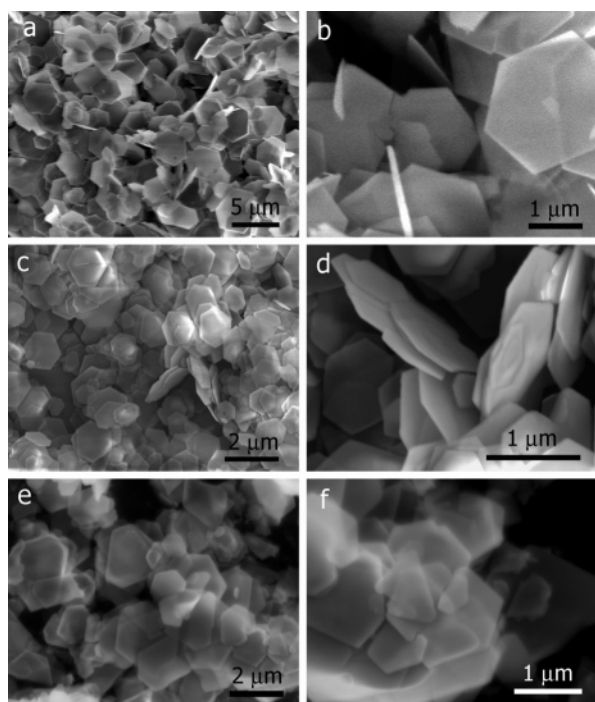
**Figure 4.** Low- and high-magnification SEM images of the α-cobalt hydroxide samples prepared with different concentrations of CoCl$_2$: (a, b) 20 mM, (c, d) 25 mM, and (e, f) 50 mM. Note that 20 mM of NaCl was contained when the CoCl$_2$ concentration was 20 mM.
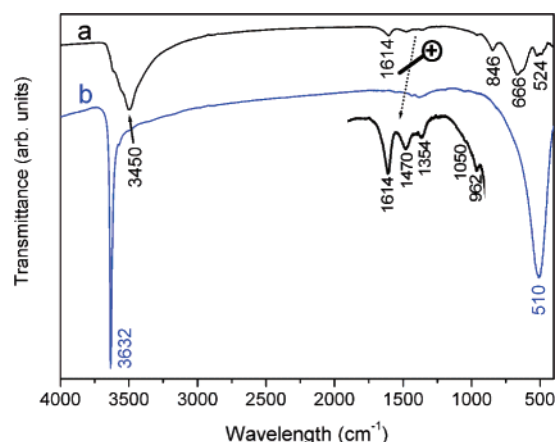


**Figure 5.** FT-IR spectra (a) α- and (b) β-Co(OH)$_2$. The inset shows a magnified view in the frequency range of 900−1900 cm$^{-1}$ for the α-Co(OH)$_2$ sample.

and CO$_3^{2-}$ ions. As a consequence of the CO$_3^{2-}$ intercalation, the as-prepared α-Co(OH)$_2$ had a slightly expanded interlayer spacing (7.95 Å) in comparison with that (7.85 Å) of the carbonate-free species.[3h] A trace amount of interlayer CO$_3^{2-}$ anions may result from the slight dissolution of CO$_2$ from air and/or the possible oxidation of HMT. The incorporation of water molecules and CO$_3^{2-}$ ions is evidenced by the FT-IR spectrum as depicted in Figure 5a. The large band centered at 3500 cm$^{-1}$ is assigned to the O−H stretching modes of interlayer water molecules and of H-bound OH groups, and the peak at 1614 cm$^{-1}$ is due to the bending mode of water molecules.[3g,f,j] The four weak bands at 846, 1050, 1354, and 1470 cm$^{-1}$ are characteristic of carbonate ions. The presence of the $\nu$1 band (1050 cm$^{-1}$) and $\nu$2 band (846 cm$^{-1}$), together with the splitting of the $\nu$3 vibration mode into two bands (1354 and 1470 cm$^{-1}$), indicates a low symmetry ($C_{2v}$) of the CO$_3^{2-}$
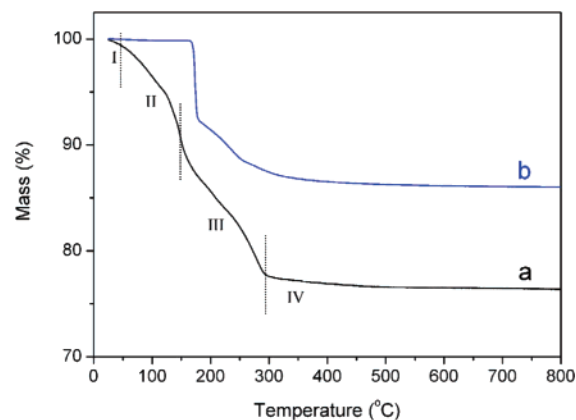
**Figure 6.** TGA data of (a) α- and (b) β-Co(OH)$_2$.

ions for the monodentate species.[10] Other absorptions below 1000 cm$^{-1}$ are associated with Co−O stretching and Co−OH bending vibrations.[3f] In the FT-IR spectrum (Figure 5b) of the β-Co(OH)$_2$ sample, in contrast, the absorption bands around 3500 and 1614 cm$^{-1}$ were not observed, suggesting the absence of interlayer water molecules. The intense and sharp band at 3632 cm$^{-1}$ is attributed to the O−H stretching mode, which is characteristic of free OH groups in brucite-like structures; the broad absorption at low-frequency region (400−600 cm$^{-1}$) is ascribed to Co−O stretching and Co−OH bending vibrations in the brucite-like octahedral sheet.[3e,f]

Figure 6a shows the TG curve of the α-Co(OH)$_2$ sample in the temperature range of 25−800 °C. The α-phase underwent weight loss of 24.4% in four steps indicated by the zones I, II, III, and IV on the graph, although they were not well-resolved. The weight loss below 50 °C (domain I) is ascribed to the removal of the adsorbed water. The weight loss (9.4%) between 50 and 145 °C (domain II) is assigned to the evaporation of the intercalated water molecules, which is in agreement with the expected value (9.3%) based on the estimated formula. Domain III ranging from 145 to 300 °C is associated with the loss of water produced by dehydroxylation of the hydroxide layers combined with the partial loss of the anionic species (CO$_3^{2-}$ and Cl$^-$). Finally, the fourth domain ending at about 600 °C can be attributed to the loss of Cl$^-$ ions. In contrast, the TG curve (Figure 6b) of the β-Co(OH)$_2$ sample showed a distinctly different profile, corresponding to the dehydration of the OH groups together with the simultaneous conversion into spinel Co$_3$O$_4$. The total weight loss (∼13.6%) is consistent with the expected value (13.6%) for the stoichiometric composition of Co(OH)$_2$. These results are in good agreement with previous reports.[8b,11]

The crystallinity of the as-prepared α- and β-Co(OH)$_2$ platelets was examined by TEM and SAED. Figure 7a and c displays the TEM images of α- and β-Co(OH)$_2$ platelets as described in Figure 2a and c, respectively. One can see that all of the platelets had a regular hexagonal platelike morphology with the angles of adjacent edges of 120°, consistent with the SEM observations. The corresponding SAED patterns (insets in Figure 7a and c) both showed perfect hexagonally arranged diffraction spots, which can be readily indexed as the two-

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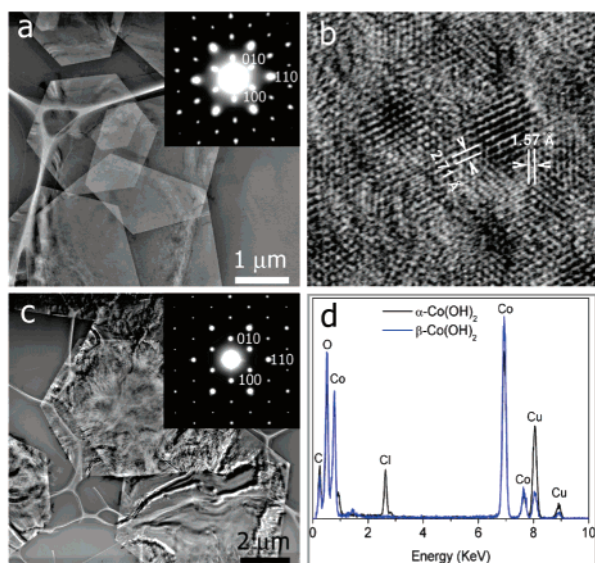
**Figure 7.** (a) TEM image of α-Co(OH)$_2$ platelets. (b) HRTEM image of a single α-Co(OH)$_2$ platelet. (c) TEM image of β-Co(OH)$_2$ platelets. (d) EDS spectra of the α- and β-Co(OH)$_2$ samples. The insets in panels a and c are the corresponding SAED patterns taken from individual platelets.

dimensional in-plane reflections. These results suggest that the platelets were lying on their {001} crystal planes and the SAED patterns were taken along the [001] zone axis direction. A representative HRTEM image (Figure 7b) of the α-Co(OH)$_2$ platelet shows clear lattice fringes of ca. 2.71 and 1.57 Å that correspond to the (100) and (110) crystal planes of the α-phase, respectively. All of these data obviously support the single-crystallinity of the α- and β-Co(OH)$_2$ platelets. To the best of our knowledge, this is the first example concerning the synthesis of single-crystal α-Co(OH)$_2$ with such a well-defined morphology. EDS measurements reveal homogeneous distribution of elements in both samples, and typical spectra are shown in Figure 7d. In the case of the α-phase sample, a strong signal of Cl appeared, and the Co/Cl ratio is calculated as about 1:0.26, well agreeing with the chemical analysis results.

**Liquid Crystalline Phase Behavior of the Colloidal Platelets.** It has long been known that colloidal suspensions of anisotropic particles (such as rods and platelets) display interesting liquid crystalline phases.[12] The previous studies revealed that the isotropic to nematic phase transition of the colloidal suspensions of anisotropic particles was largely relevant to their aspect ratios.[13] Stable liquid crystalline phases could be obtained for the platelets with larger aspect ratios even at lower platelet concentrations and/or higher polydispersities.[14] In the present study, the as-prepared α- and β-Co(OH)$_2$ platelets both had uniform sizes and considerably high aspect ratios (approximately 200 for the α-phase and 400 for the β-phase), and they could be easily dispersed into ethanol (or water) to form stable colloidal suspensions. As shown in the insets of Figure 2a and c, both bottles of suspensions exhibited clear streaming anisotropy after gently shaking, indicating the presence of free alignable platelets.[9a] Therefore, the formation of liquid crystal-

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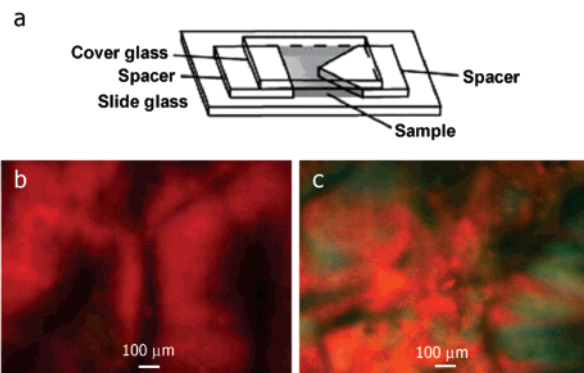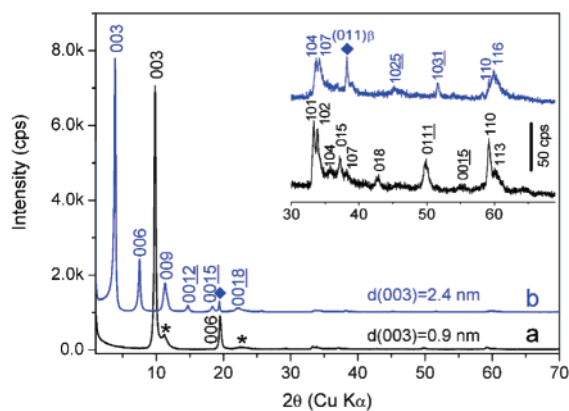


**Figure 8.** (a) Schematic illustration of the sample cell used for the optical microscope observations. (b, c) Optical microscope images of the as-prepared α- and β-Co(OH)$_2$ platelet suspensions with a concentration of about 10 g dm$^{-3}$ placed in a 0.5-mm-thick cell observed between crossed polarizers with a wave plate.

line phases is expected for the suspensions. The liquid crystallinity of the platelet suspensions was confirmed by birefringence of the samples using optical microscope observations under crossed polarizers and with a wave plate (optical retardation = 530 nm). The sample cell was self-made with a slide glass according to that illustrated in the literature,[14a] as is schematically shown in Figure 8a. To avoid the memory effect of sample injection that may possibly result in birefringence, the observations were carried out when the samples were stable (usually after 5 min of the sample injection). As shown in Figure 8b and c, the microscope images of both kinds of platelet suspensions with a particle concentration of about 10 g dm$^{-3}$ showed birefringence accompanied by interference colors due to liquid crystalline domains of the suspensions. The Schlieren textures observed in the images suggest the existence of nematic phases with submillimeter domain sizes for both kinds of platelet suspensions. The polarized optical microscope observations revealed that such nematic phases could form even at a particle concentration as low as 1 g dm$^{-3}$. This may be attributed to the large aspect ratios and relatively uniform sizes of the as-prepared platelets. It can be envisioned, as reported for gibbsite platelets,[9c] that other interesting liquid crystalline phases (such as smectic and columnar phases) may form for the α- and β-Co(OH)$_2$ platelet suspensions with a further decreased polydispersity achieved after a proper size-selection process. Further study on this topic is underway.

**Interlayer Chemistry of α-Co(OH)$_2$.** We have made attempts to prepare the α-Co(OH)$_2$ intercalated with various inorganic or organic anions by replacing CoCl$_2$ with the corresponding cobalt salts (such as nitrates and acetates) or introducing organics into the starting solution using the present synthetic route, but pure-phase α-Co(OH)$_2$ products intercalated with other inorganic anions were difficult to arrest due to a quick conversion of α to β phase during the synthesis, and the products incorporated with organic anions were poorly crystallized with turbostratic structures (see Figure S2). It is well-known that the hydrotalcite-like materials usually have rich interlayer chemistry associated with anion-exchange properties, which allows their electronic, magnetic, and optical properties to be modified with minimal change to the structure.[15] Thus, these intercalated products may be prepared via an anion-exchange process from the as-prepared α-Co(OH)$_2$ platelets in Cl$^-$ form. Representative inorganic (NO$_3^-$) and organic anions (C$_{12}$H$_{25}$OSO$_3^-$, DS) were

**Figure 9.** XRD patterns of the anion-exchanged samples: (a) $NO_3^-$ and (b) DS anions. The insets show the enlarged profiles of the patterns in high angles. The black * indicates the peaks related to the pristine $\alpha$-Co(OH)$_2$ in Cl$^-$ form, and the blue ◆ indicates the peaks corresponding to $\beta$-Co-(OH)$_2$ that formed due to the spontaneous transformation of the $\alpha$ to the $\beta$ phase.
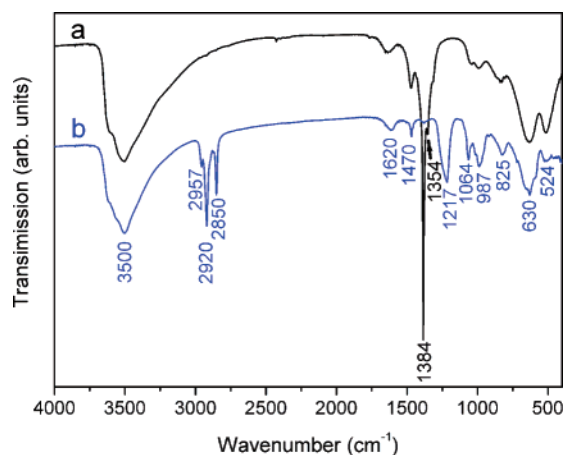


**Figure 10.** FT-IR spectra of the anion-exchanged samples: (a) $NO_3^-$ and (b) DS anions.

used for the anion-exchange experiments. At room temperature, the substitution reaction for $NO_3^-$ anions was incomplete even after 7 days of the reaction time, and no reaction occurred for DS anions. It was found that the reactions could be driven in relatively short periods at an elevated temperature. Figure 9 shows the XRD patterns of both intercalated products obtained at 90 °C after about 12 and 48 h for $NO_3^-$ and DS anions, respectively. As can be seen, the diffraction peaks of the both products were typical of $\alpha$-Co(OH)$_2$, and the *hkl* peaks (see insets of Figure 9) were still sharp and symmetric, indicating that the samples maintained high crystallinity. The basal spacing expanded from 0.8 to 0.9 nm and 2.4 nm for the intercalation of $NO_3^-$ and DS anions, respectively. The former value is compatible with that in the hydrotalcite-like phase containing $NO_3^-$ anions.[3e,k] The large basal spacing of 2.4 nm for the DS intercalated phase indicates that the long organic chains are interdigitated in the interlayer space, as the chain length of the DS is approximately 2 nm.[16] Intercalation of $NO_3^-$ and DS anions is further confirmed by FT-IR spectra (Figure 10). The

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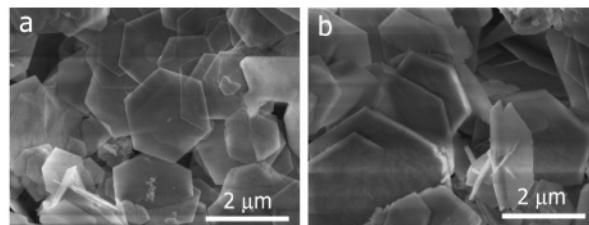(16) Sundell, S. *Acta Chem. Scand. A* **1971**, *31*, 799.

**Figure 11.** SEM images of the anion-exchanged samples: (a) $NO_3^-$ and (b) DS anions.

sharp and strong absorption peak at 1384 cm$^{-1}$ shown in Figure 10a is assigned to $\nu3$ vibration modes of $NO_3^-$ anions.[3f,l] The absorption bands at around 2850$-$2960 and 1210$-$1240 cm$^{-1}$ displayed in Figure 10b are characteristic of the aliphatic and sulfate groups of DS anions, respectively.[17] Nevertheless, two weak bands around 1354 and 1470 cm$^{-1}$ that correspond to the splitting $\nu3$ vibration mode of $CO_3^{2-}$ anions still appeared on the FT-IR spectra of the exchanged products, indicating that the $CO_3^{2-}$ ions have a very strong affinity with the Co(OH)$_{2-x}$ layers and they cannot be deintercalated. The SEM images (Figure 11) clearly show that most of particles retained the hexagonal platelike morphology. The DS intercalated platelets, however, had an increased mean thickness (about 50 nm), in good agreement with the expansion in basal spacing (from 0.8 to 2.4 nm) upon anion exchange. These results suggest that the anion exchange proceeded by a typical topotactic mechanism. A variety of intercalation $\alpha$-Co(OH)$_2$ products may be anticipated by the present anion-exchange procedure employing different inorganic and organic anions.

## Conclusion

In summary, we have succeeded in synthesizing single-crystal hexagonal platelets of $\alpha$- and $\beta$-Co(OH)$_2$ via homogeneous precipitation from a dilute CoCl$_2$ solution by hydrolysis with HMT. Cobalt hydroxide crystallites with controllable forms ($\alpha$- or $\beta$-phase) and sizes can be prepared by carefully adjusting the concentrations of both CoCl$_2$ and NaCl. Their high quality and liquid crystallinity may be advantageous for exploration of their physical and chemical properties. This synthetic method is simple and controllable, and offers great opportunities for bulk synthesis of $\alpha$- and $\beta$-Co(OH)$_2$ platelets. It is also expected that the present method may be generalized to synthesize nickel hydroxides and many other hydroxides. Furthermore, the intercalating Cl$^-$ anions of the as-prepared $\alpha$-Co(OH)$_2$ platelets can be exchanged by various inorganic or organic anions, retaining high crystallinity and original morphology.

**Supporting Information Available:** SEM images of the $\alpha$-Co(OH)$_2$ sample prepared at a high NaCl concentration. XRD pattern of DS intercalated $\alpha$-Co(OH)$_2$ samples prepared via a conventional method. This material is available free of charge via the Internet at http://pubs.acs.org.

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