γ-ray Radiation Induced Synthesis and Characterization of α-Cobalt Hydroxide Nanoparticles

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A novel synthetic route has been developed to prepare α-cobalt hydroxide with intercalated nitrate anions. It was successfully synthesized by γ-ray irradiation under simple conditions, i.e., air atmosphere, without base. Under γ-ray irradiation, it leads to the formation of layered cobalt hydroxynitrate compounds which have small crystalline size and have the role of a generator of hydroxyl anion. Structural and morphological characterizations were performed by using power X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), and high resolution transmission electron microscopy (HR-TEM). The component and thermal stability of the sample were respectively measured by Fourier transform infrared (FT-IR) spectroscopy, elemental analysis, and thermal analyses, including thermogravimetry (TG) and differential thermal analysis (DTA).

Key Words: α-Cobalt hydroxide, Layered compound, Radiolysis

Introduction

Research on layered transition-metal hydroxide materials such as nickel hydroxides and cobalt hydroxides has received considerable attention in recent years due to these materials potential applications as catalysts, supports, anion adsorbents, magnetic materials and ion exchangers as well as high-performance electrode materials of alkaline secondary batteries and supercapacitors.[1-7] Layered divalent metal hydroxides crystallize in the structure of mineral brucite, $Mg(OH)_2$. Brucite structure is composed of two hydroxide layers sandwiching a Mg^{2+} layer. These two-dimensional sheets are stacked to form a three dimensional structure that is stabilized by hydrogen bonding between the layers. This results in the stacking of charge-neutral layers of composition $[M(OH)_2; M = Mg, Co, or Ni]$ with an interlayer distance of around 4.6 Å. When some of the hydroxyl groups are missing from their positions in the layer sheets, the structure incorporates anions in the interlayer region to restore charge neutrality yielding hydrotalcite-like structures with the general formula $[M(OH)_{2-x}] \cdot (A^{n-})_{x/n} (A^{n-} = Cl^-, NO_3^-, or CO_3^{2-})$. The interlayer spacing of these structures varies from 6.9 to 9.2 Å depending upon the size and orientation of anion.[8]

Among a variety of layered transition-metal hydroxide materials, cobalt hydroxides have attracted interest due to their layered structure with large interlayer spacing, their high electrochemical redox activity, and the possibility of enhanced performance depending upon preparation conditions.[9] Cobalt hydroxides are well-known to crystallize in two polymorphic forms, α and β. The first one is an isostructural with hydrotalcite-like compounds while the second is a brucite-like structure with a stoichiometric phase of the composition $Co(OH)_2$.[10] The α-phase cobalt hydroxide is theoretically expected to exhibit higher electrochemical activity as compared to the β-one because of its turbostratically disordered structure.[11] There are several

methods to prepare the α-cobalt hydroxides by electrochemical and chemical syntheses including urea and ammonia precipitation as well as a hydrolysis agent.[12-14] In those cases, stabilizer or basic condition are generally needed. Recently, radiation techniques have been utilized as a catalyst to solve those problems in material synthesis.[15]

In the present study, we have developed a novel synthetic route to generate the α-cobalt hydroxide from cobalt nitrate hexahydrate isopropanol solution using a ^{60}Co gamma ray with a dose rate of 25 kGy/h without stabilizer or chemical agent. The physicochemical characterizations of obtained cobalt hydroxide have been carried out, along with the comparison of physicochemical properties by conventional chemical method.

Experimental

Sample preparation. Cobalt(II) nitrate hexahydrate and 2-propanol were obtained from Aldrich in analytical grade and were used without further purification. Decarbonated water was prepared by boiling deionized water from a Milli-Q water purification system. 3 g (4.6 mmol) of cobalt(II) nitrate hexahydrate was dissolved in 30 mL of 2-propanol and then the sample solution was radiated with gamma rays using ^{60}Co source as a function of time (4, 6, 8 and 10 hours). Gamma ray radiation was carried out in a ^{60}Co Gamma cell irradiator with a dose rate of 25 kGy/h provided by the Korea Atomic Energy Research Institute. After radiation, the obtained product was centrifuged, washed several times with decarbonated water and dried in a vacuum.

For comparison of physicochemical properties with obtained cobalt hydroxide obtained by radiolysis, α-cobalt hydroxide was also prepared by urea hydrolysis method.[16] In typical synthesis, 18 g (27.6 mmol) of cobalt (II) nitrate hexahydrate was mixed with 2 g (33.3 mmol) of urea and 2 mL of water in a beaker and the mixture was placed inside a pre-heated oven at 140 °C for

2 h. It was occasionally stirred until it turned viscous at which stage the mixture was removed from the oven and cooled to room temperature. The resulting powder was collected by filtration, washed with distilled water to remove excess free Co^{2+} ions, and dried at room temperature.

Sample characterization. The crystal structures of the obtained samples were studied by powder X-ray diffraction (XRD) measurements using Ni filtered Cu Kα radiation (1.5418 Å) with a graphite diffracted beam monochromator. The patterns were recorded at an operating voltage of 40 kV and current of 20 mA. The chemical compositions of samples were determined by performing elemental analysis (CE-Instruments-EA-1110) and thermal gravimetric-differential thermal analysis (Rigaku TAS-100). Thermal analysis was carried out to check the thermal behavior of as-prepared samples under air condition where the heating rate was fixed at 10 °C/min. High resolution-transmission electron microscopy (HR-TEM) was carried out using a JEOL JEM-2100F and field emission-scanning electron microscopy (FE-SEM) was performed with a JEOL JSM-6700F microscope. Fourier transform-infrared (FT-IR) spectra were obtained by a Varian FTS 800 FT-IR spectrometer with the standard KBr disk method. The IR analysis was performed in the frequency range of 400 ~ 4000 cm⁻¹.

Results and Discussion

Generally, radiolysis was used to prepare metals such as silver $[E^0 (Ag^+/Ag) = 0.79$ V, NHE] and copper $[E^0 (Cu^{2+}/Cu) = 0.33$ V, NHE] by reduction of metal ions because electron arising radiolysis of the solvent plays the role of a strong reducing agent. However, it is a difficult to prepare cobalt metal due to its low redox potential $(E^0 (Co^{2+}/Co) = -0.28$ V, NHE).[17] As a result of radiation into cobalt nitrate solution, α-cobalt hydroxide was prepared. The species generated from 2-propanol and coordinated water molecules in cobalt nitrate hexahydrate by radiation are shown below.
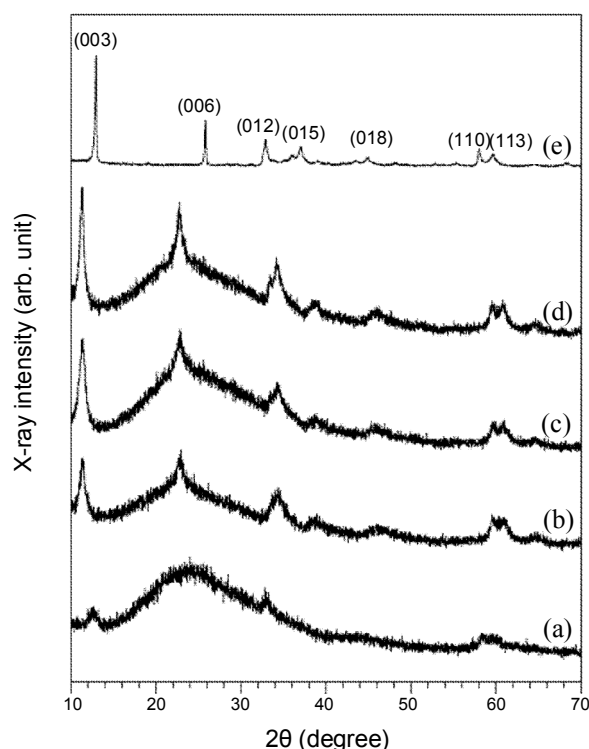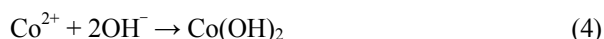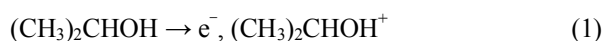
$$(CH_3)_2CHOH \rightarrow e^-, (CH_3)_2CHOH^+ \qquad (1)$$

$$H_2O \rightarrow H\cdot, OH\cdot \qquad (2)$$

$$e^- + OH\cdot \rightarrow OH^- \qquad (3)$$

$$Co^{2+} + 2OH^- \rightarrow Co(OH)_2 \qquad (4)$$

Figure 1. Powder XRD patterns of α-cobalt hydroxide by radiolysis method depending upon the radiation times [(a) 4 h, (b) 6 h, (c) 8 h and (d) 10 h] and urea hydrolysis method (e).

e^- and OH radical were produced by the radiolysis of 2-propanol and hydrate.[18] Then hydroxide might be formed from e^- and OH radical. Therefore, α-cobalt hydroxide was synthesized with cobalt ion and hydroxide in the absence of any additive chemical agent.

Figure 1 shows the powder X-ray diffractograms of the cobalt hydroxides by radiolysis method depending upon the radiation time [(a) ~ (d)] and conventional wet chemical method (e). All of the patterns match well with that assigned to α-Co(OH)₂ (JCPDS: file no. 46 - 0605) and the cobalt hydroxide obtained by chemical method shows relatively high crystallinity. The chemical formula and the lattice parameter obtained from the least-squares fitting analyses of the cobalt hydroxides are summarized in Table 1. The indices $(-h + k + l = 3n)$ clearly indicate a rhombohedral symmetry. In case of radiation for 8 hours, the lattice

Table 1. XRD analysis results and chemical formulas for as-prepared cobalt hydroxide samples

Preparation method	Radiation time (h)	Lattice parameters[a]		Interlayer spacing (Å)[b]	Size in c-axis (Å)[c]	Chemical formula[d]
		a (Å)	c (Å)			
Radiolysis	4	3.17	21.35	7.07	67.4	$Co(OH)_{1.38}(NO_3)_{0.62}\cdot1.58H_2O$
	6	3.01	23.26	7.79	49.3	$Co(OH)_{1.50}(NO_3)_{0.50}\cdot1.46H_2O$
	8	3.10	23.40	7.83	95.3	$Co(OH)_{1.42}(NO_3)_{0.58}\cdot1.75H_2O$
	10	3.11	23.51	7.86	102.3	$Co(OH)_{1.47}(NO_3)_{0.53}\cdot1.83H_2O$
Urea hydrolysis	-	3.18	20.75	6.86	-	$Co(OH)_{1.62}(NO_3)_{0.38}\cdot0.11H_2O$

[a]The lattice parameters were obtained from the least-squares fitting analyses. [b]Interlayer spacings were calculated from 003 diffraction patterns. [c]Mean crystallite size calculated from full width of half-maximums of (003) peaks. [d]Chemical formula were estimated from the thermal and elemental analysis results.
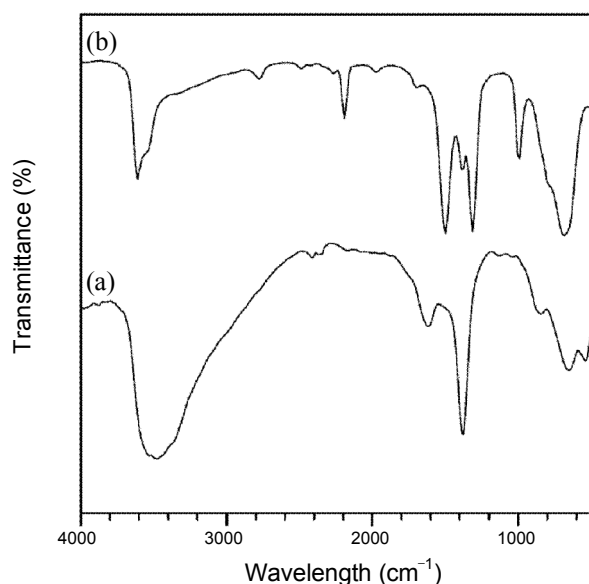
Figure 2. Fourier transform infrared spectra of α-cobalt hydroxide by radiolysis method with 10 hours radiation time (a) and urea hydrolysis method (b).

parameters of α-Co(OH)$_2$ were refined to be $a = 3.100038$ Å and $c = 23.40407$ Å compared with conventional chemical synthetic α-Co(OH)$_2$ with $a = 3.181343$ Å and $c = 20.75105$ Å. In practice, the lattice parameter a corresponds to the average cation-cation distance within a layer, while parameter c corresponds to several times the thickness of basal spacing. The first parameter depends mostly upon the ionic radii of the metal cation, while the second one depends on the size and orientations of the intercalated anion and water molecules in the interlayer space.[19] In this regard, the slight difference of c parameters clearly suggests that the compound contains different amount of interlayer water or different orientation of the intercalated anions. The third diffraction peak has the typical broad "sawtooth" shape indicating that layer stacking in the obtained samples by radiolysis must be rather loose and defective, leading to a turbostratic structure.[20] It is well known that the main difference between the α-form and β-form of cobalt hydroxide resides in the stacking of the layers. Upon radiation time increase, the crystallinity of the resulting cobalt hydroxides becomes higher, suggesting that the total radiation dose can influence to extent the crystallization during the radiolysis process, while the full width at half maximum (FWHM) of X-ray reflections slightly increases. Assuming that the X-ray line broadening is essential due to the size effect, the estimated particle size falls into the range of 50 ~ 100 nm from the Debye-Scherrer formula.[21]

The FT-IR spectra of cobalt hydroxide samples are shown in Figure 2. The infrared absorption (curve b) of α-Co(OH)$_2$, obtained by chemical methods is given for comparison and discussion. All samples show broad and intense bands centred around *ca.*3500 cm^{-1} corresponding to the O-H stretching vibrations of the gallery water molecules and hydrogen-bonded hydroxyl groups in cobalt hydroxides. But the sharp peak, as shown by curve (b) in Figure 2, attributed to the O-H stretching mode, disappears in cases of the radiolysis method due to their
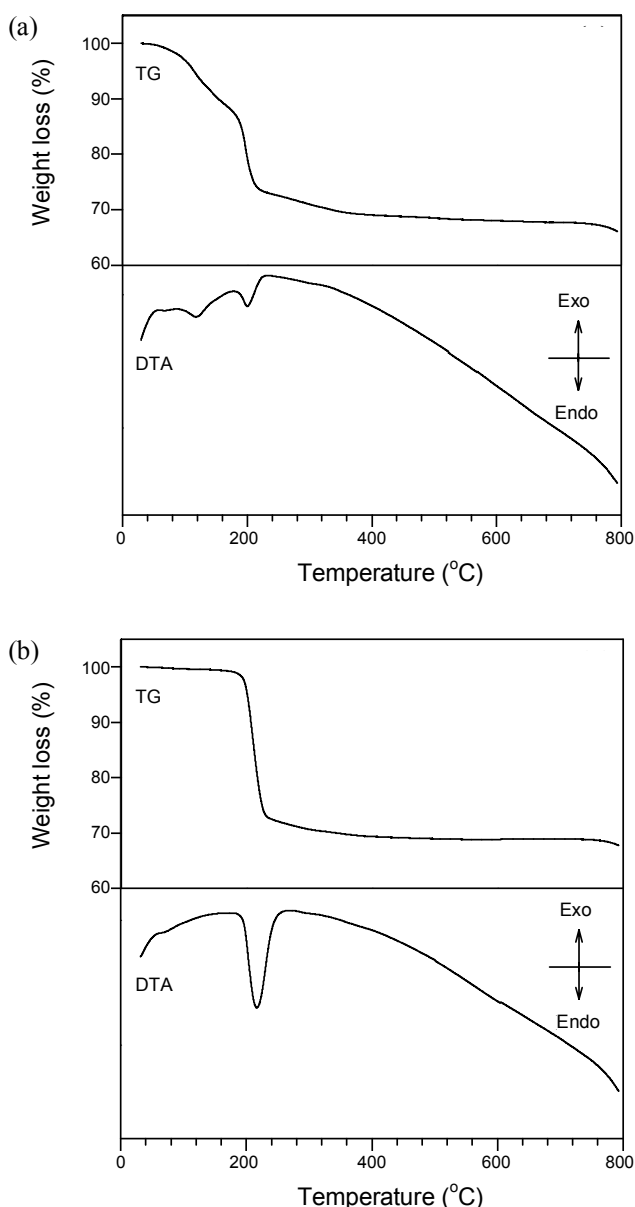

Figure 3. TG & DTG curves for α-cobalt hydroxide by radiolysis method with 10 hours radiation time (a) and urea hydrolysis method (b).

relative small size and poor crystallinity. Evidence for nitrate incorporation could be found in the sharp peak at 1378 cm^{-1}, which could be attributed to vibrational (ν3) modes of NO$_3^-$ intercalated in the layers. In the low wavenumber region below 800 cm^{-1}, the absorptions are associated with Co-O stretching and Co-OH bending vibrations. The band at 650 cm^{-1} can be assigned to the δ (Co-O-H) and the absorption band at about 530 cm^{-1} can be assigned to the ν (Co-O) stretching vibrations. In case of using urea hydrolysis method (Figure 2b), the bands due to the nitrate groups are seen in the 1600 cm^{-1} ~ 1000 cm^{-1}. Figure 2b shows three strong absorption peaks (ν1: 1310 cm^{-1}; ν3: 1002 cm^{-1} and ν4: 1501 cm^{-1}) that have been assigned to the strongly bound nitrate group. The absorption band at 2200 cm^{-1} was assigned to the stretching vibration of the intercalated isocyanate ion (NCO$^-$), which was one of the products of urea hydrolysis,
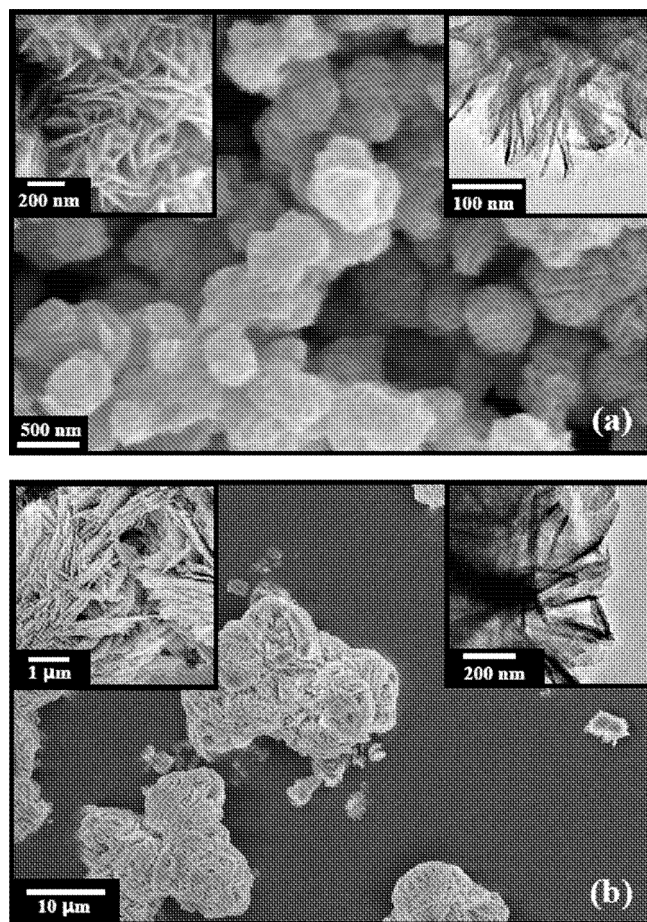
Figure 4. FE-SEM and HR-TEM images of α-cobalt hydroxide by radiolysis method with 10 hours radiation time (a) and urea hydrolysis method (b).

and therefore could be expected to be included in the interlayer region during synthesis.[22]

Figure 3 represents the TG-DTA curves for the α-cobalt hydroxide obtained by γ-irradiation for 10 hours (a) and using urea hydrolysis method (b), respectively. The hydroxyl vacancies would then be occupied by water molecules to be yield slabs of composition. This is so-called structural water would be a fraction of the total water contents, which include the absorbed and intercalated water molecules as well. The dehydration was expected to be two step process, with the absorbed and intercalated water loss.[23] The α-cobalt hydroxide obtained by radiolysis underwent total weight loss of 33.9% through three steps in the graph (Figure 3a). The first step weight loss (1.8%) below 85 ^{o}C was ascribed to the removal of the absorbed water and isopropanol solvent on the surface of α-cobalt hydroxide. The second weight loss (9.1%) between 85 ^{o}C and 160 ^{o}C was assigned to the evaporation of the intercalated water molecules and the third weight loss (19.6%), which ranged from 160 ^{o}C to 350 ^{o}C was associated with the loss of water produced by dehydroxylation of the hydroxide layers and decomposition of the intercalated nitrate molecules.[24] Otherwise, the α-cobalt hydroxide prepared by urea hydrolysis method shows predominately weight loss in the temperature ranged from 170 ^{o}C to 210 ^{o}C because it has a relatively small amount of water molecules

between the interlayer spaces of cobalt hydroxide sheets.

Figure 4 represents the FE-SEM and HR-TEM images for prepared layered α-cobalt hydroxide materials using radiation and urea hydrolysis method. The FE-SEM images of the sample obtained by γ-ray radiation with 10 hours radiation time are shown with uniform size and crystal shapes and plate-like nanostructures are observed clearly. The plate has a uniform thickness with a size of about ~8 nm and the particles morphology is flowerlike architectures with a radius of around 500 nm. A closer observation of the structure is shown in Figure 4(a) inset image (left), which indicates that each flower was composed of a nanosized plate. These plates were connected to each other to build the 3D flowerlike structure. This shows good agreement with the results from the TEM image. On the other hand, the sample obtained by urea hydrolysis consists of large sized particles (> 20 μm) and an irregular morphology distinguished from the samples using γ-ray radiolysis method.

Conclusions

The radiolysis method is an effective method for preparation of nanosized α-cobalt hydroxide. Compared to conventional chemical methods, the radiolysis has diverse advantages due to echo-friendly simplicity of reaction without base and heat, homogeneous morphologies, and uniform particle sizes with nanometer domain. The obtained α-cobalt hydroxide had uniform 3D flowerlike shapes composed of aggregates of flakes which are built from nanocrystalline plates. This 3D flowerlike structure of α-cobalt hydroxide has been expected to have enhanced electrochemical properties such as α-nikel hydroxide.[25]

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