

Electron Beam Mediated Simple Synthetic Route to Preparing Layered Zinc Hydroxide

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We have developed a novel and eco-friendly synthetic route for the preparation of a two-dimensional layered zinc hydroxide with intercalated nitrate anions. The layered zinc hydroxide nitrate, called 'zinc basic salt', was, in general, successfully synthesized, using an electron beam irradiation technique. The 2-propanol solutions containing hydrated zinc nitrate were directly irradiated with an electron-beam at room temperature, under atmospheric conditions, without stabilizers or base molecules. Under electron beam irradiation, the reactive OH· radicals were generated by radiolysis of water molecules in precursor metal salts. After further radiolytic processes, the hydroxyl anions might be formed by the reaction of solvated electrons and the OH· radical. Finally, the $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ was precipitated by the reaction of zinc cation and hydroxyl anions. Structure and morphology of obtained compounds were characterized by powder X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), and high resolution transmission electron microscopy (HR-TEM). The chemical components of the products were determined by Fourier transform infrared spectroscopy (FT-IR) and elemental analysis (EA). The thermal behavior of products was studied by thermogravimetric (TG) and differential thermal analysis (DTA).

Key Words : Layered hydroxide salts, Zinc hydroxide nitrate, Radiolysis, Electron beam

Introduction

In recent years, layered materials have attracted considerable research interests because of their lamellar-type crystal structure and the possibility of producing nanohybrids by intercalating or ion-exchanging inorganic or organic species between interlayer spaces. The layered materials are widely applied to fields such as catalysis, electrochemistry, separation technology, and medical science.¹⁻⁴

Among the various two-dimensional layered materials, layered hydroxide salts (LHS) have been of great interest due to their simple synthetic process and unique anion-exchange properties. The structure of LHS is based on the mineral brucite ($Mg(OH)_2$) structure and is composed of positively charged hydroxide layers with charge-compensating anions in the interlayer spaces. Positive charges on layers are developed from under-coordination or mixed coordination geometries of intralayer cations. Therefore, counter-anions are required to stabilize the electrostatic charge of layers. The general formula of an LHS is $M^{2+}(OH)_{2-x}(A^{n-})_{x/n} \cdot mH_2O$, where M^{2+} is the metallic cation and A^{n-} a counter-anion (e.g., NO_3^- , Cl^- , CO_3^{2-} , or SO_4^{2-}).⁵

Zinc hydroxide nitrate (ZHN), $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$, is one of the LHSs in which each layer is composed of a main Zn^{2+} sheet, with cations octahedrally coordinated by hydroxyl anions. Unlike other brucite-like structured LHSs, a quarter of the octahedral sites are vacant, surrounded by zinc tetrahedrons whose bases share hydroxyls with the octahedral sheet while water molecules occupy the apexes, and the nitrate counter-anions are free in the interlayer

spaces.^{5,6} Several methods are generally used to prepare the ZHN; these methods include chemical precipitation with basic solution or urea hydrolysis, hydrothermal reaction, and electrodeposition. In those cases, the use of a strong base or an organic stabilizer is required and, in some cases, thermal or electrical energy is needed.⁷⁻¹¹

Recently, radiation techniques, such as electron beam or gamma-ray irradiation, are showing their potentials as new, effective and eco-friendly methods with which to synthesize nanosized materials; they might be applied to various systems. Many scientists have reported the preparation of metal crystallite, metal oxide, metal sulfide and alloy using radiation techniques combined with other synthetic methods.²²⁻²⁴ However, there are only a few reports of the preparation of LHS materials using the radiation method.^{25,26}

In this report, we developed a novel synthetic route to synthesize the ZHN from zinc nitrate hexahydrate in 2-propanol using the electron beam without base molecules, stabilizers, or heat treatment. The physicochemical characterizations of the obtained ZHNs were carried out, as compared with properties of ZHN prepared by conventional chemical method. The anion exchangeability the ZHNs synthesized by radiolysis and chemical methods was also tested using sodium dodecyl sulfate (SDS).

Experimental Section

Materials. Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 98%, Aldrich), 2-propanol (C_3H_8O , 99.5%, Aldrich), SDS ($NaC_{12}H_{25}SO_4$, $\geq 99\%$, Aldrich) and sodium hydroxide

(NaOH, $\geq 93\%$, Ducksan chemical) were purchased and used without further purification.

Sample Preparation.

Synthesis of the Layered ZHNs by Electron Beam Irradiation: The experiments by electron beam irradiation were carried out without reducing or stabilizing agents, generally used for the preparation of ZHN. Sample solutions were prepared by dissolving 9.19 g (30.9 mmol) of zinc (II) nitrate hexahydrate into 90 mL of 2-propanol. The solutions were transferred to petri dishes and irradiated by an electron beam with 100-250 kGy doses at room temperature, under atmospheric conditions. The electron beam irradiation was performed at a dose rate of 1 kGy/10 s in a linear electron beam accelerator (UELV-10-10S) provided by the Korea Atomic Energy Research Institute. After electron beam irradiation, sample solutions were centrifuged and washed several times with decarbonated water; white powders were obtained by drying in air, at room temperature.

Preparation of ZHN by Precipitation in Alkaline Solution: For comparison of the physicochemical properties of the obtained ZHNs by radiolysis (*e.g.*, ZHN-250), ZHN (ZHN-chem) was also prepared by conventional chemical precipitation methods, in alkaline solution.^{8,14} Fifty mL of 0.75 M NaOH solution were added, drop-wise, into 20 mL of 3.5 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ aqueous solution at room temperature, with vigorous stirring. The solution was filtered, and the white powder was washed with decarbonated water and then dried in air.

Anion Exchangeability Test. The anion exchangeability of layered ZHNs obtained by radiolysis and chemical methods was tested using SDS.^{7,20,21} ZHN-250 and ZHN-chem powders (62.5 mg, 0.1 mmol) were respectively added to 15 mL decarbonated water solution containing 57.7 mg (0.1 mmol) of SDS, and each mixture was stirred at room temperature for 4 days. The reaction solutions were centrifuged and washed several times with distilled water; the resultant powders (ZHN-250-DS and ZHN-chem-DS) were dried in an oven at 60 °C.

Characterization. The crystal structures of the obtained samples were studied by powder X-ray diffraction (XRD) measurement, using Ni filtered Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å, Rigaku) with a graphite diffracted beam monochromator. The patterns were recorded at an operating voltage of 40 kV and a current of 30 mA. The chemical compositions were determined by performing elemental analysis (Thermo Electron-FLASH EA1112) and thermogravimetric-differential thermal analysis (TG-DTA, Rigaku TAS-100). By TG-DTA performance, thermal behavior of samples was checked under the N_2 condition, where the heating rate was fixed at 10 °C/min from room temperature to 800 °C. Phase purity and chemical components were confirmed by Fourier transform-infrared spectroscopy (FT-IR, Varian FTS 800 FT-IR) with the standard KBr disk method. The FT-IR analysis was performed in the frequency range of 400-4000 cm^{-1} at a resolution of 2 cm^{-1} . The morphology of the samples was investigated using high resolution-transmission electron microscopy (HR-TEM, JEOL JEM-3010) with an accelerat-

ing voltage of 300 kV and field emission-scanning electron microscopy (FE-SEM, JEOL JSM-6700F). Each product was dispersed in water, and a drop of the dispersion was placed on a carbon coated copper grid (Carbon Type-B, 200 mesh) for HR-TEM measurement and a silicon wafer for FE-SEM measurement and allowed to dry in air.

Results and Discussion

Powder XRD and Elemental Analyses. Figure 1 shows the powder XRD patterns of the layered ZHNs prepared by the electron beam irradiation method, depending upon the radiation doses [(a)-(d)] and ZHN by chemical precipitation method (e). All the XRD patterns are in agreement with previously published data (JPCDS file No. 72-0627, $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$) and exhibit high crystallinity with monoclinic crystal system.^{8,10-12} The basal spacings of the samples calculated from each (200) diffraction peak at around 9.0° (2θ) are approximately 9.76-9.82 Å. In the case of ZHN-250, the lattice parameters were refined to $a = 19.56$ Å, $b = 6.27$ Å, $c = 5.55$ Å and $\beta = 93.12^\circ$ and these values are almost identical to those of ZHN-chem ($a = 19.56$ Å, $b = 6.26$ Å, $c = 5.54$ Å and $\beta = 93.15^\circ$); they are also consonant with previously reported data.^{13,14,20} In the XRD patterns of radiolysis samples (Fig. 1(a)-(d)), the crystallinity becomes higher as a function of electron beam irradiation doses. It is obvious that the total radiation doses can influence the extent of crystallization during the radiolysis process, and crystallinity can be controlled by adjusting radiation doses. The chemical formulas obtained from elemental and thermal analysis and the lattice parameters of the samples are summarized in Table 1. The chemical formulas show the presence of small amounts of carbonate ion in all samples;

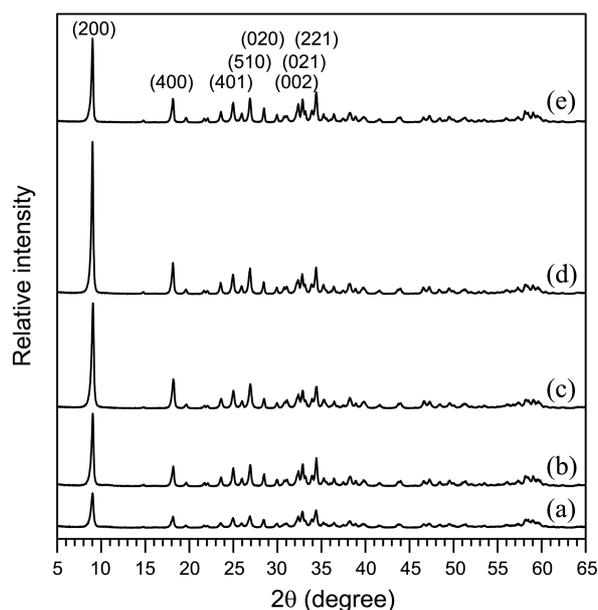


Figure 1. Powder XRD patterns of the layered ZHNs prepared by radiolysis method depending upon the radiation doses [(a) 100 kGy, (b) 150 kGy, (c) 200 kGy and (d) 250 kGy] and conventional chemical method (e).

Table 1. XRD analysis results and chemical formulas for the layered zinc hydroxide nitrate samples

Preparation method	Sample	Interlayer spacing (Å) ^a	Size in <i>a</i> -axis (nm) ^b	Lattice parameters ^c			Chemical formula ^d
				<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	
Radiolysis (electron beam)	ZHN-100	9.80	24.30	19.61	6.27	5.54	Zn ₅ (OH) ₈ (NO ₃) _{1.42} (CO ₃) _{0.29} ·2H ₂ O
	ZHN-150	9.78	30.35	19.56	6.27	5.54	Zn ₅ (OH) ₈ (NO ₃) _{1.54} (CO ₃) _{0.23} ·2H ₂ O
	ZHN-200	9.76	27.69	19.53	6.26	5.53	Zn ₅ (OH) ₈ (NO ₃) _{1.46} (CO ₃) _{0.27} ·2H ₂ O
	ZHN-250	9.82	35.46	19.56	6.27	5.55	Zn ₅ (OH) ₈ (NO ₃) _{1.66} (CO ₃) _{0.17} ·2H ₂ O
Precipitation in alkaline solution	ZHN-chem	9.80	34.46	19.56	6.26	5.54	Zn ₅ (OH) ₈ (NO ₃) _{1.76} (CO ₃) _{0.12} ·2H ₂ O

^aInterlayer spacings were calculated from 200 diffraction patterns. ^bMean crystallite size were calculated from the full-width of half-maximums of (200) peak. ^cThe lattice parameters were obtained from the least-squares fitting analyses. ^dChemical formulas were estimated from the thermal and elemental analysis results.

this is attributed to the fact that the intercalated nitrate ions are substituted into the carbonate ions because of the reaction conditions under ambient air. The average primary particle sizes of the samples were estimated to be about 24.30–35.46 nm by Scherrer's equation from the (200) diffraction peak of XRD patterns.

FT-IR Analysis. Figure 2 shows the FT-IR spectra of the ZHN samples obtained using radiolysis (a) and chemical precipitation (b). In both spectra, there are no significant differences in peak position and chemical composition. All the samples exhibit obviously broad and intense bands in the 3600–3400 cm⁻¹ region corresponding to the O-H stretching vibrations, which originate from the three types of structurally different hydroxyl groups. The sharp band at around 3580 cm⁻¹ can be assigned to stretching vibrations of hydroxyl groups on lattice. The vibration of the lattice hydroxyl groups, which is linked by hydrogen bonds with water and NO₃⁻ anion molecules, is located at approximately 3500 cm⁻¹. The broad band below 3500 cm⁻¹ is attributed to

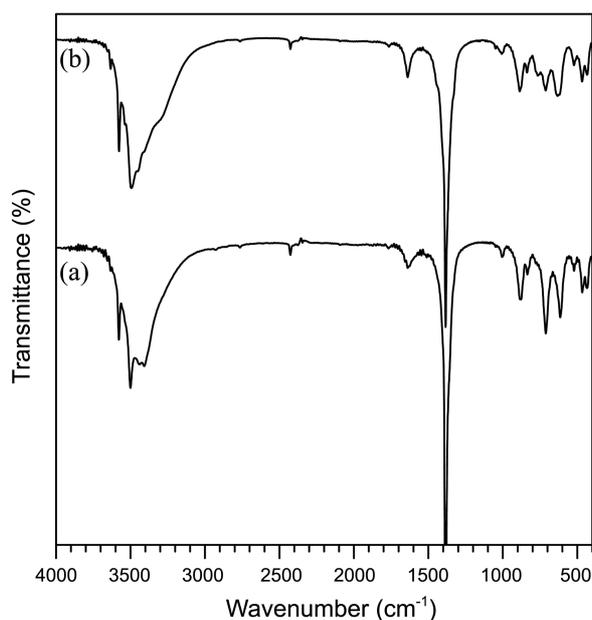


Figure 2. FT-IR spectra of ZHNs prepared by radiolysis method, with 250 kGy electron beam doses (a) and conventional chemical method (b).

hydroxyl groups of water molecules placed in ZHN interlayer spacing or is physisorbed onto the layer.^{12–16} The peak of stretching vibration of hydroxyl groups on lattice in ZHN-250 shows more clearly distinguished than that of ZHN-chem. It is indicate that the OH groups of ZHN-250 are more exactly located in correct lattice point and are more strongly bound than ZHN-chem. The band at 1638 cm⁻¹ is assigned to the bending mode of the water molecule. In the case of layered ZHN, an intercalated nitrate anion is uncoordinated with Zn²⁺ and has *D*_{3h} symmetry.^{14–17} The sharp peak at 1381 cm⁻¹ is assigned to the *v*₃ stretching vibrational mode of NO₃⁻, which is the characteristic peak of a nitrate group. Also, other vibration bands of nitrate ions appear at 836 cm⁻¹ (*v*₂) and 711 cm⁻¹ (*v*₄), except at the *v*₁ mode because *v*₁ vibration of NO₃⁻ with *D*_{3h} symmetry are inactive in IR.¹⁷ In the low wavenumber region, there are lattice vibrations of Zn-O bonds at approximately 433 and 467 cm⁻¹ and Zn-O-H bending vibration is located at 1006 cm⁻¹. The absorption peaks of the intercalated carbonate ions do not appear in FT-IR spectra, due to their small mole fraction in the sample and their slightly similar peak positions to nitrate ion.^{12,15}

TG-DTA Analysis. Thermal behaviors of ZHNs obtained by radiolysis and chemical precipitation were checked through TG-DTA performance, and the results were represented in Figure 3. The ZHN-250 (Fig. 3(a)) underwent a total weight loss of 35.05% with the four endothermic reactions. The first weight loss (5.62%) occurred below 112 °C and was ascribed to the removal of structural and physisorbed water molecules. In the second step (at 157 °C), the ZHN structure began to collapse, due to the dehydroxylation of the lattice, and Zn₃(OH)₄(NO₃)₂ and ZnO remained at the end of this step. At 189 °C (third weight loss), Zn(NO₃)₂ and ZnO were formed through the dehydration of Zn₃(OH)₄(NO₃)₂ and partial decomposition of nitrate anion to nitric acid. In the final weight loss step, above 208 °C, the Zn(NO₃)₂ decomposed into ZnO by generating NO₂, NO and O₂.^{13,14,18} The asymmetric peaks (second and third weight loss steps) of the DTA curve indicate that the dehydroxylation process occurs in temperature ranges partially overlapping with the following dehydration and decomposition processes.¹⁴ The weight loss of the dehydroxylation and the decomposition process totals

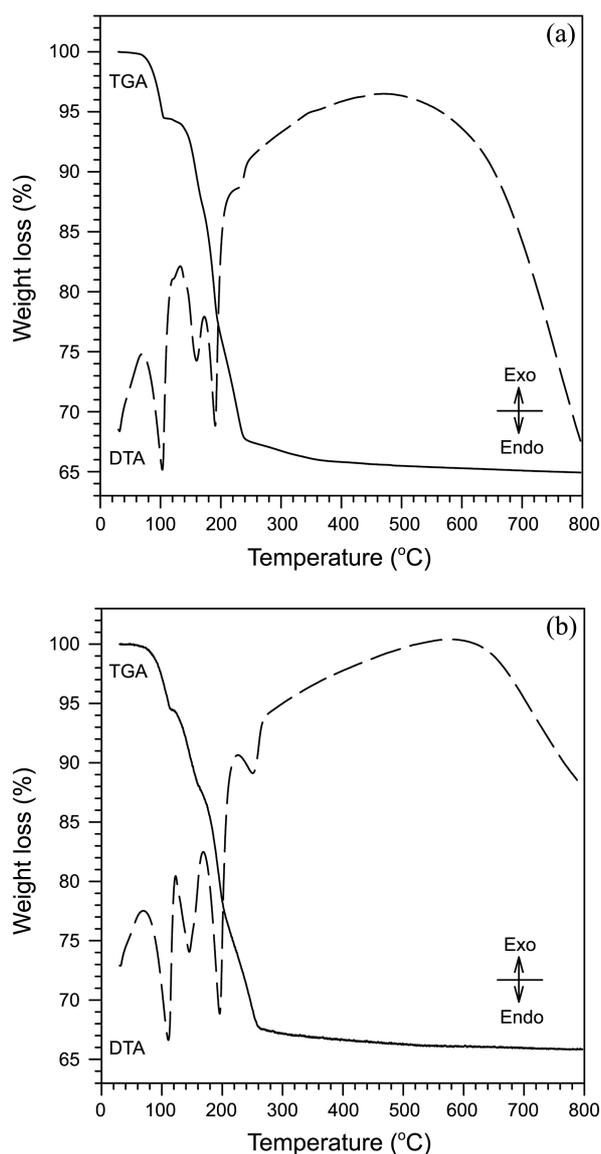


Figure 3. TG & DTA curves for layered ZHN prepared by (a) radiolysis method with 250 kGy electron beam doses (ZHN-250) and (b) precipitation method in alkaline solution (ZHN-chem).

about 29.43%, and this result is in agreement with theoretical value (28.89%).^{12,14} The endothermic peak of the carbonate decomposition is not present in TG-DTA curves because of its slight weight percentage (about 2%), and the reaction temperature overlapped with zinc nitrate decomposition (decomposition process of carbonate occurs approximately at 250 °C).⁸ In the case of the ZHN-chem sample (Fig. 3(b)), total weight loss is 34.11% and the weight loss process experienced, overall, the same process as ZHN-250. The weight loss of the first step is 5.61% (below 119 °C) and that of the dehydroxylation and decomposition step is 28.5%. The difference in endothermic temperature of second step (about 14 °C) of two samples is attributed from the difference between the crystallinity of two samples. This result is coincided with the results of electron diffraction patterns and FTIR data.

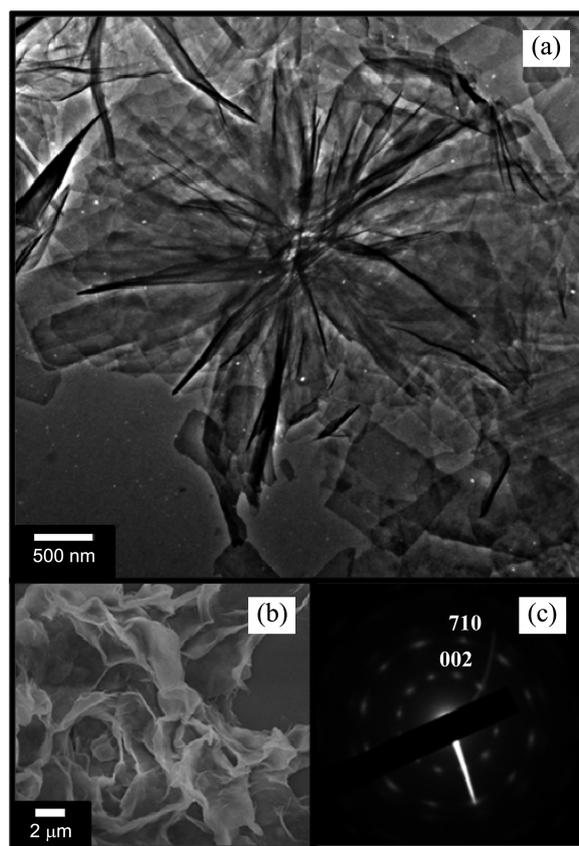


Figure 4. HR-TEM (a), FE-SEM (b) images and electron diffraction patterns (c) of the layered ZHN prepared by radiolysis method, with 250 kGy electron beam doses (ZHN-250).

HR-TEM and FE-SEM Analyses. HR-TEM and FE-SEM images for layered ZHNs synthesized by electron beam irradiation and chemical precipitation methods are shown in Figures 4 and 5, respectively. The HR-TEM image in Figure 4(a), ZHN-250 appear as well developed plate shapes, and the size of each plate is about 0.5-2 μm. The result of the FE-SEM measurement (b) also shows fluttering platelet morphology, which stacks layer upon layer and is coincident with the result of HR-TEM. Although a few layers overlap, electron diffraction patterns in Figure 4(c) show clear diffraction spots, indicating the high crystallinity of the ZHN-250 sample, as shown in XRD pattern. On the other hand, the sample prepared by chemical precipitation method (ZHN-chem) shows irregular platelet-like morphology in HR-TEM measurement (Fig. 5(a)). It seems the *a*-axis direction (*100*) of the plate is mainly perpendicular to the electron beam on the Cu grid rather than the horizontal orientation, unlike the main orientation of ZHN-250 and most layered materials. From HR-TEM (a) and FE-SEM (b) images, the plate size of ZHN-chem sample appears smaller than that of ZHN-250.

Anion Exchange Property Test with Dodecyl Sulfate Ions. The anion exchangeability test of obtained samples was performed by intercalation reaction of dodecyl sulfate ion (DS). The structures of the obtained ZHN-250-DS and ZHN-chem-DS powders were characterized using XRD, and

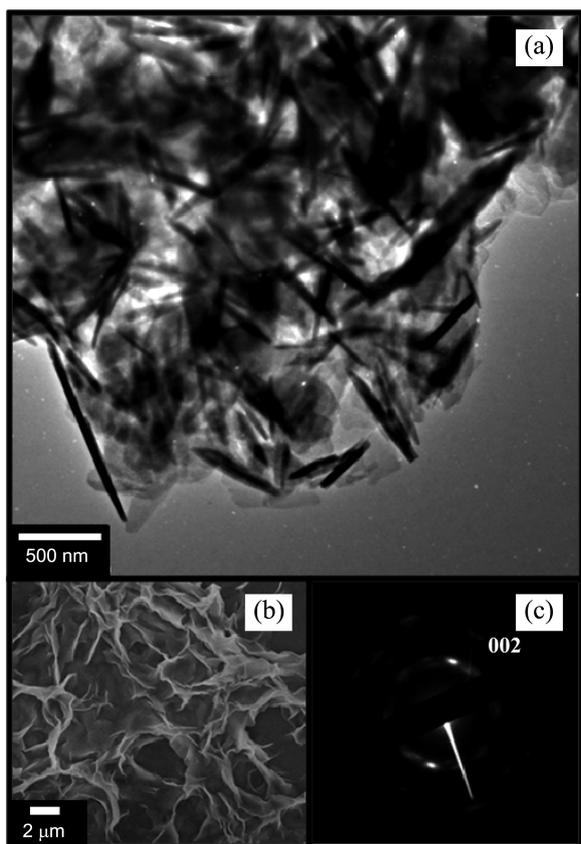


Figure 5. HR-TEM (a), FE-SEM (b) images and electron diffraction patterns (c) of the layered ZHN, prepared by conventional precipitation method in alkaline solution (ZHN-chem).

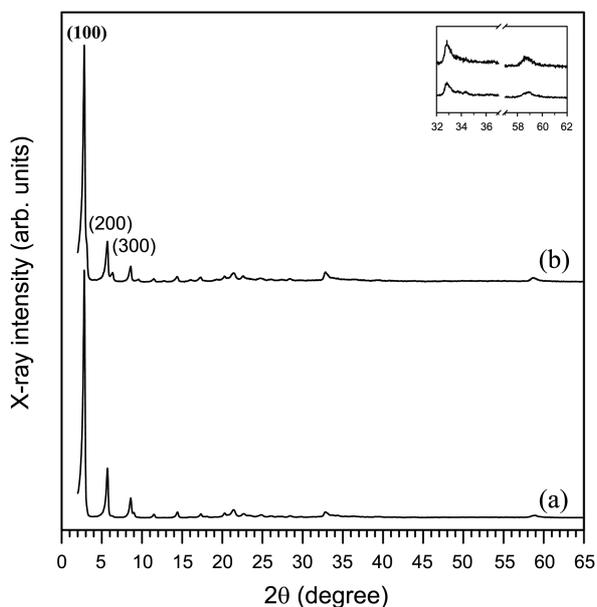


Figure 6. Powder XRD patterns of dodecyl sulfate intercalated ZHN-250 (a) and ZHN-chem (b).

the results are shown in Figure 6. The XRD patterns of two samples show a series of $h00$ reflections, indicating extensive order along the layer stacking direction.^{7,20,21} The basal spacings of ZHN-250-DS (a) and ZHN-chem-DS (b), calcu-

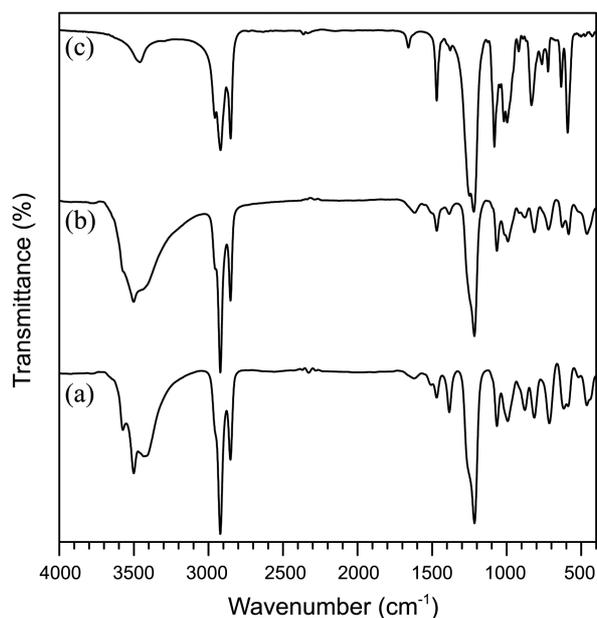


Figure 7. FT-IR spectra of dodecyl sulfate intercalated ZHN-250 (a) and ZHN-chem (b), and sodium dodecyl sulfate (c).

lated from the first $h00$ reflection at around 2.8° in two-theta, are approximately 31.2 Å and 31.0 Å, respectively. From these results, we could primarily confirm that the nitrate ions were exchanged by dodecyl sulfate ions. Meanwhile, there are slightly asymmetric peaks at $\sim 33^\circ$ and $\sim 59^\circ$ indicating that partially turbostratic disordered layers exist. The pattern of ZHN-chem-DS shows another phase of the intercalated DS, with a basal spacing of 26.5 Å. This additional phase was generated from tighter packing of dodecyl sulfate ions in the interlayer space.⁷ On the other hand, the pattern of ZHN-250-DS appears as clearly as the mono-phase of intercalated DS ion. The difference between the two patterns can be indirect evidence that the charge density of ZHN, prepared by radiolysis, is different from that of the conventionally prepared ZHN.

We also analyzed the composition of DS ion intercalated ZHNs by FT-IR spectroscopy. In the FT-IR spectrum of ZHN-250-DS (Fig. 7(a)), the vibration band of nitrate, approximately 1380 cm^{-1} is still but has reduced intensity. This indicates that the nitrate ions were nearly completely exchanged for DS ions. Strong peaks at 2957, 2930 and 2851 cm^{-1} are attributed to C-H stretching vibration modes of the alkyl chains of the intercalated DS ions. Another strong band at 1224 cm^{-1} is assigned to the S=O stretching vibrations of DS.^{7,20} In the spectrum of ZHN-chem-DS (b), the O-H vibration peaks, which are located in the $3600\text{--}3400\text{ cm}^{-1}$ region, changed broadly, accompanying the disappearance of sharp peaks in the lattice hydroxyl group. This might be due to the occurrence of deformation or collapse of lattice during the anion exchange reaction. On the other hand, ZHN-250-DS still shows the three types of hydroxyl groups because of the high crystallinity of the original ZHN-250 sample. As these results indicate, we verified that ZHN prepared by electron beam irradiation has anion exchange-

ability.

Conclusion

We demonstrate that radiolysis using electron beam irradiation is an effective method for preparation of layered zinc hydroxide nitrate. The ZHN-250 sample by radiolysis shows relatively higher crystallinity than that of chemical precipitation methods. Compared to conventional chemical methods, radiolysis has various advantages, such as the eco-friendly reaction due to no use of chemical agents, simple processes, and the possibility to control crystallinity by adjusting the electron beam dose. Also, the ZHN prepared by electron beam irradiation has anion exchangeability, a general property of layered metal hydroxide compounds.

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