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Morphology and size control of 513 MHSH, $Mg(OH)_2$ from sea bittern using H_2SO_4 and NH_4OH

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513 MHSH (Magnesium Hydroxide Sulfate Hydrate) and $Mg(OH)_2$ were synthesized using a domestic resource, sea bittern, as a Mg precursor instead of conventional reagents. Sea bittern contains a large amount of Ca^{2+} ions, which can be efficiently removed using sulfuric acid. We synthesized them using the obtained $MgSO_4$ solution from sea bittern. By adding ammonia to the $MgSO_4$ solution to synthesize plate-like $Mg(OH)_2$ and adjusting the $Mg(OH)_2/MgSO_4$ ratio by adjusting the amount of ammonia, needle-like 513 MHSH were synthesized. In addition, the synthesized hexagonal plate-like $Mg(OH)_2$ was grown to a size of 50 to 400 nm by hydrothermal reaction. The conditions for synthesizing the needle-like 513 MHSH were found by the addition of sulfuric acid. The synthesized 513 MHSH and $Mg(OH)_2$ were characterized by X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).

Keywords: Sea bittern, $Mg(OH)_2$, Magnesium, $CaSO_4$, $MgSO_4$ solution.

Introduction

Magnesium hydroxide sulfate hydrate [abbreviated MHSH, $xMg(OH)_2{\cdot}yMgSO_4{\cdot}zH_2O$ (x-y-z phase;)] has various structures depending on the ratio of $Mg(OH)_2$, $MgSO_4$ and H_2O [1-3]. MHSH whiskers exist in various forms such as 513 MHSH ($5Mg(OH)_2{\cdot}MgSO_4{\cdot}3H_2O$), 517 MHSH ($5Mg(OH)_2{\cdot}MgSO_4{\cdot}7H_2O$), 512 MHSH ($5Mg(OH)_2{\cdot}MgSO_4{\cdot}2H_2O$) and 212 MHSH ($2Mg(OH)_2{\cdot}MgSO_4{\cdot}2H_2O$) [4-8]. 513 MHSH whiskers, a needle-like inorganic material, have attracted attention due to their practical applicability, including their use in resins, fillers and fibrous composites and as a reinforcement material [9-12]. Due to the SO_4^{2-} ion-bonded structure between the $Mg(OH)_2$ layered structures, 513 MHSH can be used as a flame retardant because of the release of water molecules at temperatures higher than the usual dehydration temperature under fire conditions. 513 MHSH forms a structure in which layered $Mg(OH)_2$ are bonded by SO_4^{2-} ions, and the bonding with sulfate ions causes water molecules to be released at a higher temperature than the general dehydration temperature in fire conditions [13-16].

513 MHSH whiskers can be obtained by using various starting materials, such as MgO, $MgSO_4$, $MgCl_2$, or $Mg(OH)_2$ [17-19]. 513 MHSH synthesis is possible by adjusting the $MgSO_4$/MgO ratio through a hydrothermal reaction [20-22]. Pure 513 MHSH can be obtained with $MgSO_4$ and ammonia, but the use of a strong base, such as NaOH, easily forms $Mg(OH)_2$ and interferes with the formation of the 513 MHSH [23]. Furthermore, because $Mg(OH)_2$ and $MgSO_4$ are easily modified under acidic/basic conditions, 513 MHSH can be synthesized using $Mg(OH)_2$ precursors and sulfuric acid [3, 24]. Our group previously investigated the synthesis and morphologies of 513 MHSH by adjusting the ratio of the reagent precursor MgO/$MgSO_4$ and applied the results to find the conditions for synthesizing 513 MHSH using acid and base catalysts, H_2SO_4 and ammonia [3, 21-24].

Sea bittern removes Na^+ ions from seawater through an ion exchange membrane, and Mg^{2+} ions are present at relatively high concentrations, so it is easy to extract Mg^{2+} ions from sea bittern [25]. However, because sea bittern contains Ca^{2+} ions at a higher concentration compared to seawater, Ca^{2+} ions must be removed efficiently to synthesize high-purity magnesium compounds [25]. Adding sulfuric acid to sea bittern can remove Ca^{2+} ions by taking advantage of the solubility difference between $MgSO_4$ and $CaSO_4$. Because the relatively low-soluble calcium sulfate ($CaSO_4$, 2.55 g/L) is precipitated and the highly soluble magnesium sulfate ($MgSO_4$, 351 g/L) remains as ions in the solution, the two substances can be easily separated. After the removal of the Ca^{2+} ions from the sea bittern using sulfuric acid, needle-like 513 MHSH and plate-like $Mg(OH)_2$ were synthesized by adjusting the amount of basic precipitant in the purified $MgSO_4$ solution.

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Experimental procedures

Materials

We used sea bittern (Hanju Salt, Korea) as the Mg precursor. Sodium hydroxide (NaOH, Daejung Chem., Korea) and sulfuric acid (10% H_2SO_4, Daejung Chem., Korea) were used to extract the $MgSO_4$ and $Mg(OH)_2$. Sulfuric acid (95% H_2SO_4, Samchun Chem., Korea) and ammonium hydroxide (28% NH_4OH, Daejung Chem., Korea) were used without further purification as the catalyst in the synthesis process for the 513 MHSH. An aqueous solution of the precursor systems was prepared with the appropriate quantities of reagents in distilled water, using various synthesis conditions to obtain the 513 MHSH whiskers. Then, the morphology and structure were examined by Scanning Electron Microscopy (SEM, Model JSM-6390, JEOL, Japan), Transmission Electron Microscopy (TEM, Model CM 200, Philips, Netherlands) and powder X-Ray Diffraction (XRD, Model D/Max 2500, Rigaku, Japan). Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Model SPECTRO ARCOS, SPECTRO Analytical Instruments, Germany) and X-ray Fluorescence (XRF, Model S1 TITAN, Bruker, USA) were used to identify the components of the raw materials and the solution.

Synthesis of the 513 MHSH

In general, 513 MHSH is synthesized using a hydrothermal method. Previously, we synthesized 513 MHSH adjusting the molar ratio of the $MgSO_4$ and MgO, using the reaction of the single precursor $MgSO_4$ and NH_4OH (basic catalyst) and the reaction with $Mg(OH)_2$ and H_2SO_4 (acid catalyst). These experiments utilized the reagents MgO and $MgSO_4$ to synthesize high-purity 513 MHSH by adjusting the pH, using ammonia and sulfuric acid as catalysts. We investigated the effect of pH, a critical factor in 513MHSH synthesis, and selected NH_4OH, a weak base with better pH control than NaOH because elevated pH levels favored the formation of $Mg(OH)_2$ over 513 MHSH [21, 23].

It is difficult to produce uniform 513 MHSH whiskers because plate-like $Mg(OH)_2$ particles were formed in high concentrations of OH^- due to the interaction between Mg^{2+} and OH^- [26, 27]. The amount of SO_4^{2-} ions is also an important factor in whisker growth because it affects the one-dimensional growth of MHSH, and if the amount of SO_4^{2-} ions is too small, Mg^{2+} ions combine with OH^- ions rather than SO_4^{2-} ions to form $Mg(OH)_2$ instead of 513 MHSH [22].

In this work, we prepared $MgSO_4$ and $Mg(OH)_2$ using sea bittern as the Mg precursor instead of the reagent $MgSO_4$ and $Mg(OH)_2$ and synthesized high-quality 513 MHSH whiskers using NH_4OH and H_2SO_4 as the catalyst to control the pH in two ways. In the first method, sulfuric acid was added to the sea bittern to form a $MgSO_4$ solution, and NH_4OH (basic catalyst) was added to the solution to adjust the pH conditions to synthesize the 513 MHSH. In the second method, 513 MHSH was synthesized by adding sulfuric acid as a catalyst to $Mg(OH)_2$, which was prepared by adding excess base to the $MgSO_4$ solution derived from the sea bittern. Sea bittern is concentrated seawater and is rich in Mg^{2+} ions but also contains high levels of other metal ions, including Ca^{2+} ions, due to the concentration process. Because the presence of Ca^{2+} ions interrupts the synthesis of high-purity Mg compounds, Ca^{2+} removal from the sea bittern is necessary. We added sulfuric acid and removed them by precipitation in the form of calcium sulfate ($CaSO_4$). Calcium sulfate ($CaSO_4$) is precipitated due to its low solubility, while $MgSO_4$ remains dissolved because of its high solubility [28].

Figure 1 presents a schematic diagram showing the synthesis process of 513 MHSH from sea bittern using basic and acidic catalysts, including the Ca^{2+} removal process by adding sulfuric acid and the shape and size control through pH adjustment. In Route 1, after removing the Ca^{2+} ions with sulfuric acid, an appropriate amount of NH_4OH was added to the $MgSO_4$ solution to synthesize the 513 MHSH through hydrothermal synthesis. In Route 2, an excess amount of NH_4OH was added to the $MgSO_4$ solution at room temperature to obtain 50 nm hexagonal magnesium hydroxide.

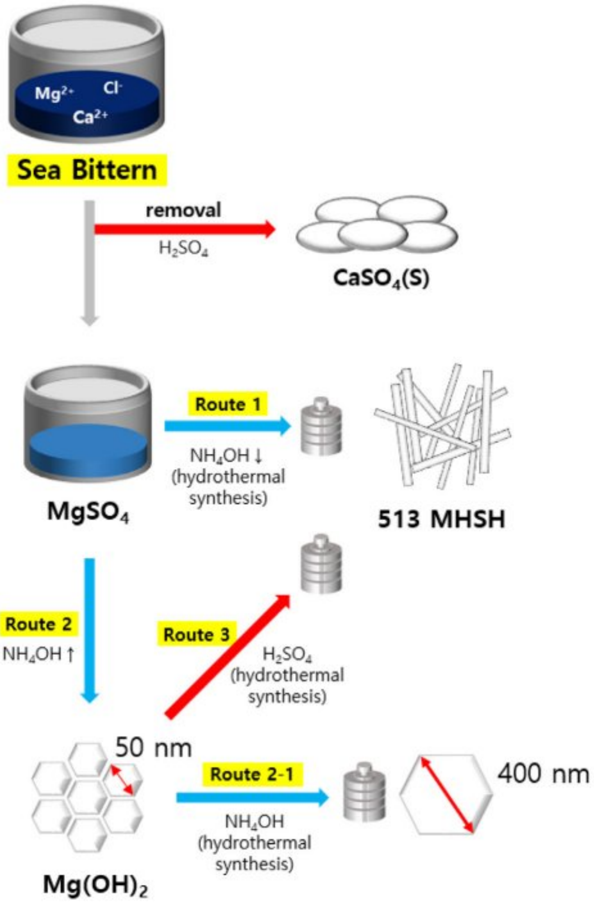

Fig. 1. Schematic diagram of the synthesis of 513MHSH from sea bittern.

Table 1. Reaction condition of 513MHSH

Sample	Starting materials	NH_4OH (mL)	H_2SO_4 (mL)	Reaction time (h)	Reaction Temperature (℃)	Phase
1	$MgSO_4$	65	-	48	180	$MgSO_4$
2		70				$Mg(OH)_2$
3		80				$Mg(OH)_2$
4	$MgSO_4$ (30% evaporation)	46	-	48	180	513 MHSH
5		50				$Mg(OH)_2$
6		70				$Mg(OH)_2$
7	$Mg(OH)_2$	-	10	24	180	$Mg(OH)_2$+513MHSH
8			20			$Mg(OH)_2$+513MHSH
9			30			513 MHSH

The particle size increases from 50 to 400 nm when hydrothermally synthesized in a basic condition in Route 3. We synthesized 513 MHSH using a hydrothermal reaction with a sulfuric acid catalyst in Route 3 and magnesium hydroxide in Route 2.

This study was done in three steps: 1) the removal process of Ca^{2+} from sea bittern using sulfuric acid to prepare a $MgSO_4$ solution, 2) the synthesis process of 513 MHSH and $Mg(OH)_2$ by adjusting the amount of basic precipitant, and 3) the synthesis process of 513 MHSH and $Mg(OH)_2$ by adjusting the pH of the synthesized $Mg(OH)_2$ solution. In the Ca^{2+} removal process, Ca^{2+} ions in the sea bittern are precipitated as $CaSO_4$ by reacting sulfuric acid with the sea bittern. The 513 MHSH synthesis can be synthesized using two catalysts. The detailed experimental conditions for the synthesis of 513 MHSH are summarized in Table 1.

Extraction of $MgSO_4$ using sulfuric acid

Adding sulfuric acid to sea bittern removes Ca^{2+} ions and creates a $MgSO_4$ solution.

$$\text{Sea bittern} + H_2SO_4 \rightarrow MgSO_4 + CaSO_4{\cdot}2H_2O\downarrow + 2H^+$$

$$MgSO_4 \rightarrow Mg^{2+} + SO_4^{2-}$$

190 g of 10% H_2SO_4 were added to 100 g of sea bittern and vigorously stirred for 30 minutes. Adding an excess amount of sulfuric acid to sea bittern ensured sufficient SO_4^{2-} ions in the form of $MgSO_4$. After stirring, the precipitated $CaSO_4$ was separated from the $MgSO_4$ solution via centrifugation. This method involves removing Ca^{2+} ions by reacting them with SO_4^{2-} ions to form calcium sulfate ($CaSO_4$) through precipitation. Because $MgSO_4$ exists as ions, it can act as a good precursor for the synthesis of Mg-based materials. In addition, because the ratio and amount of $MgSO_4$ /MgO are important, the remaining $MgSO_4$ solution was heated at 100°C for 2 hours to evaporate 30% of the solution to control the molar concentration of $MgSO_4$ solution based on previous experiments [20-22].

Synthesis of 513 MHSH using a basic catalyst and $MgSO_4$ solution from sea bittern

When ammonia was added to the $MgSO_4$ solution extracted from the sea bittern, some of the Mg^{2+} ions reacted with the OH^- ions and were converted to $Mg(OH)_2$. $Mg(OH)_2$ combined with SO_4^{2-} ions caused the formation of 513 MHSH.

$$MgSO_4 + 2NH_4OH \leftrightarrow Mg(OH)_2 + (NH_4)_2SO_4$$

$$Mg(OH)_2 \leftrightarrow Mg^{2+} + 2OH^-$$

$$6Mg^{2+} + 10OH^- + SO_4^{2-} + 3H_2O \rightarrow 5Mg(OH)_2{\cdot}MgSO_4{\cdot}3H_2O$$

NH_4OH (4 M) solution (65-80 mL) was added to the $MgSO_4$ solution prepared from sea bittern at room temperature to produce the whiskers. In the subsequent hydrothermal procedure, the solution was transferred to a Teflon-lined autoclave with a 100 mL capacity. The autoclave was maintained at 180 °C for 48 h in a drying oven and then naturally cooled down to room temperature. The obtained products were centrifuged, washed with deionized water and dried in air at 80 °C for one day. Based on the previous studies that increased Mg^{2+} selectivity facilitates 513 MHSH formation, we did the experiment by adjusting the concentration of the $MgSO_4$ solution obtained from the sea bittern [20-22]. To increase the Mg^{2+} concentration, 46-70 mL of 4 M NH_4OH were added after approximately 30% of the $MgSO_4$ solution had been evaporated, given its critical role in 513 MHSH synthesis.

Synthesis of $Mg(OH)_2$ plates from sea bittern

$Mg(OH)_2$ was synthesized by adding ammonia to $MgSO_4$ obtained from the sea bittern under room temperature and pressure conditions. When a basic precipitant was added to the generated $MgSO_4$ solution, OH^- ions combined with the Mg^{2+} ions in the sea bittern to precipitate in the form of $Mg(OH)_2$.

$$MgSO_4 + 2NaOH \rightarrow Mg(OH)_2\downarrow + 2Na^+ + SO_4^{2-}$$

$$MgSO_4 + 2NH_4OH \rightarrow Mg(OH)_2\downarrow + 2NH_4^+ + SO_4^{2-}$$

For the synthesis of $Mg(OH)_2$, De-Ca sea bittern was added at a molar ratio of 1:2 to a basic precipitant, NaOH or NH_4OH, and sufficiently stirred at 300 rpm for 2 hours. The obtained products were centrifuged at 8000 rpm for 10 minutes, washed with deionized water and dried in air at 80 °C for one day to obtain $Mg(OH)_2$ as a powder [25].

Formation of $Mg(OH)_2$ plate particles up to 400 nm

First, 0.5 g of $Mg(OH)_2$ were dissolved in 10 mL of 2M NH_4OH deionized water and then ultra-sonicated for 5 minutes. Then, the solution was transferred to a 25 mL capacity Teflon-lined autoclave. The autoclave was maintained at 180 °C for 1-24 hours in a drying oven and then allowed to cool naturally to room temperature. The obtained products were centrifuged, washed with deionized water and dried in air at 60 °C for one day.

Synthesis of 513 MHSH using a sulfuric acid catalyst and $Mg(OH)_2$ from sea bittern

$Mg(OH)_2$ at the desired concentration (4 M) was dissolved in 50 mL of deionized water and subjected to ultra-sonication for 5 min. After 10 to 30 mL of 5 M H_2SO_4 solution was added, the solutions were transferred to a 100 mL capacity Teflon-lined autoclave. The autoclave was maintained at 180 °C for 48 hours in a drying oven and then allowed to cool naturally to room temperature. The obtained products were centrifuged, washed with deionized water and dried in air at 60 °C for one day.

Results and Discussion

Chemical compositions of the sea bittern

Sea bittern is a solution where sodium ions (Na^+) in seawater are partially removed by an ion exchange membrane, resulting in a solution primarily composed of magnesium ions (Mg^{2+}). To determine the components of the sea bittern, Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analysis was performed. Table 2 shows the ion content results of the sea bittern used in the experiment. The analysis results indicate that the sea bittern contains 3.65 wt% of Mg^{2+} ions, and it also has a high concentration of other impurities such as Ca^{2+} and K^+ ions. The reason is both Mg^{2+} ions and impurities like Ca^{2+} ions from seawater were concentrated when passing through the ion exchange membrane. For use as a Mg precursor, Ca^{2+} ions must be removed.

Table 2. ICP-OES data of sea bittern of company H

Sample	Component (wt %)					
	Cl^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	K^+	Na^+
Sea bittern	16.82	0.006	1.3	3.65	4.21	2.65

Synthesis of 513 MHSH

In Table 1, samples 1-3 were prepared by adding 190 g of H_2SO_4 to the sea bittern, followed by the addition of $MgSO_4$ and 65-80 ml of 4M NH_4OH. Samples 4-6 were prepared by adding 190 g of H_2SO_4 to the sea bittern and then adding 46-70 ml of 4M NH_4OH to a solution of $MgSO_4$ that had been concentrated to approximately 30% through evaporation. Samples 1-6 were stirred for 2 hours and then subjected to hydrothermal synthesis at 180 °C for 48 hours in a Teflon vessel. Samples 7-9 were prepared by mixing the $Mg(OH)_2$ solution with H_2SO_4, followed by stirring and then undergoing hydrothermal synthesis at 180 °C for 24 hours. The precipitate was collected by centrifugation, washed with distilled water, and dried at 60 °C.

Analysis of $MgSO_4$ solution extracted from the sea bittern

A $MgSO_4$ solution was obtained by adding sulfuric acid to the sea bittern, effectively removing the Ca^{2+} impurities from the Mg precursor. This process utilized the difference in the solubility of $MgSO_4$ and $CaSO_4$. When we added ammonia to the $MgSO_4$ solution from which the precipitated $CaSO_4$ was removed, we obtained $Mg(OH)_2$.

The addition of H_2SO_4 to sea bittern reduced the Ca^{2+} ion content by over 90% due to the precipitation of $CaSO_4$ as an insoluble salt from the reaction between the Ca^{2+} and SO_4^{2-} ions and the Mg/Ca ratio increased. The removal of Ca^{2+} ions through the reaction with SO_4^{2-} ions enhances the selectivity for Mg^{2+}, facilitating the formation of 513 MHSH. Additionally, the addition of sulfuric acid to sea bittern provides SO_4^{2-} ions, which is an important factor in the formation of 513 MHSH. The ratio of $MgSO_4$/MgO also has a significant effect on the formation of 513 MHSH. The concentration of sea bittern was adjusted based on our previous studies [27]. The $MgSO_4$ solution derived from the sea bittern was concentrated by approximately 30% through evaporation to increase the Mg^{2+} ion content and facilitate the synthesis of 513 MHSH.

Influence of NH_4OH (basic catalyst) on the Formation of 513 MHSH

Figure 2 shows the XRD patterns of the products obtained by varying the amount of NH_4OH added to the $MgSO_4$ solution prepared by treating sea bittern with H_2SO_4. It can be confirmed that when 70 to 80 ml of 4M NH_4OH was added to the original sea bittern solution, a single-phase $Mg(OH)_2$ peak was observed (Fig. 2a, 2b). When less than 65 ml of NH_4OH was added, no product formed. To address this result, some of the $MgSO_4$ solutions were evaporated to match the concentration of $MgSO_4$ to the previously published 513 MHSH synthesis conditions [20]. The concentration of the $MgSO_4$ solution from the sea bittern was compared with the previous synthesis data, revealing that NH_4OH in a high concentration of $MgSO_4$ significantly affects the shape of the 513 MHSH whiskers. Thus, the $MgSO_4$

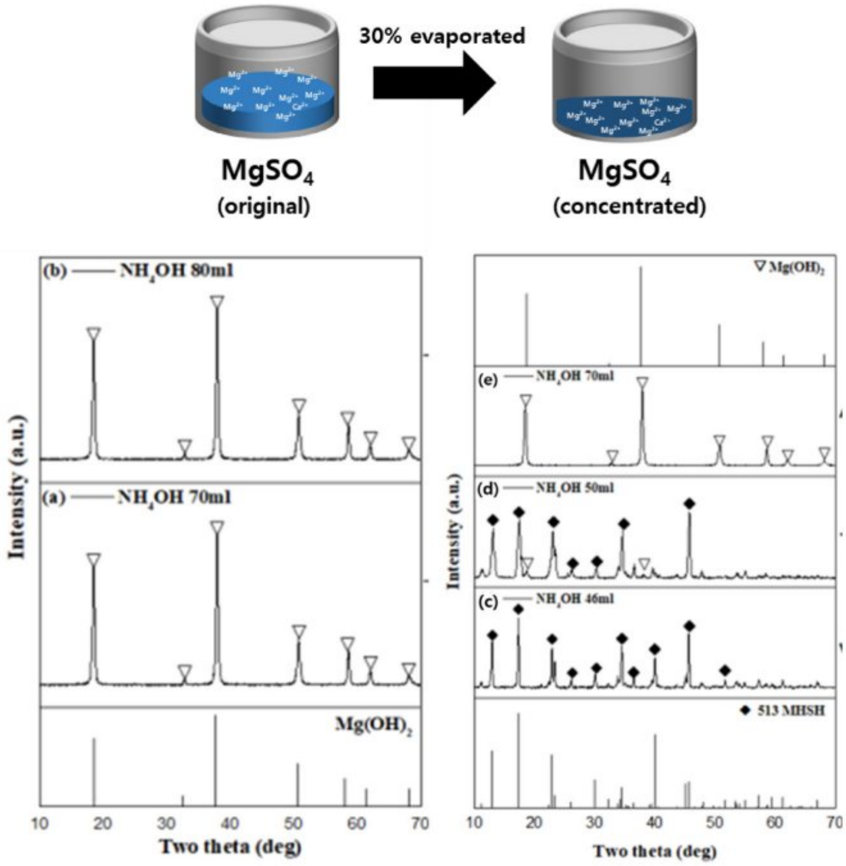

Fig. 2. XRD patterns of the products synthesized at different $MgSO_4$ concentration and ammonia: (a) 70 ml, (b) 80 ml at original $MgSO_4$ [left], (c) 46 ml, (d) 50 ml, (e) 70 ml at evaporated $MgSO_4$ [right].

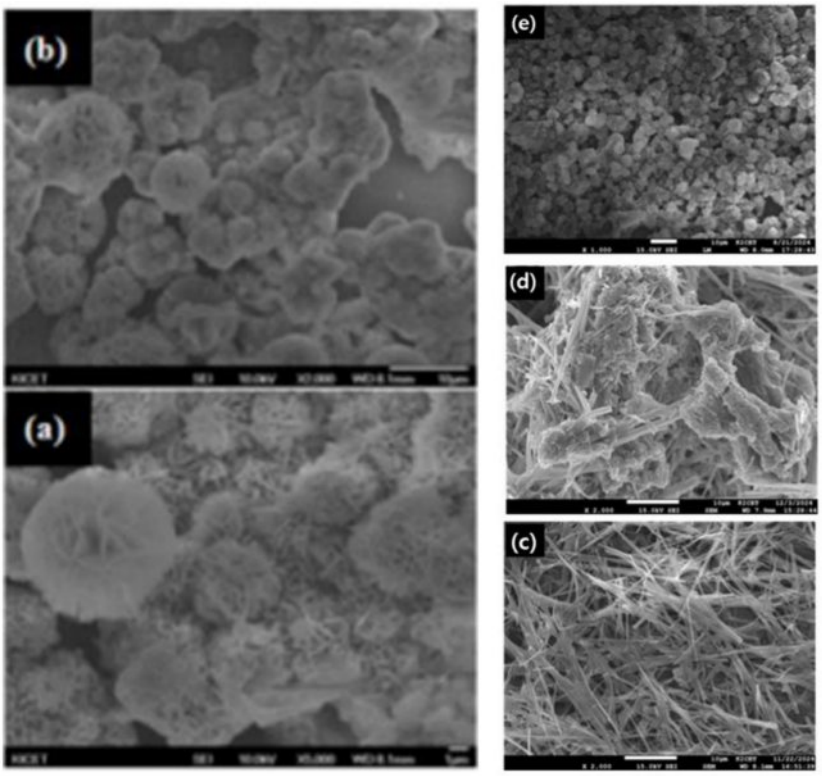

Fig. 3. SEM images of the products synthesized at different $MgSO_4$ concentration and ammonia: (a) 70 ml, (b) 80 ml at original $MgSO_4$ [left], (c) 46 ml, (d) 50 ml, (e) 70 ml at evaporated $MgSO_4$ [right].

concentration from the sea bittern was too low to produce Mg compounds. When using a concentrated $MgSO_4$ solution by evaporating 30% of the original $MgSO_4$ solution, we could obtain the 513 MHSH by adjusting the amount of ammonia.

SEM confirmed these results. Fig. 3 shows the SEM images of the products formed by controlling the amount of NH_4OH added to the $MgSO_4$ solution derived from the sea bittern treated with H_2SO_4. Fig. 3a and 3b show SEM images of aggregated plate-like $Mg(OH)_2$ particles formed from the original sea bittern, while the morphology of products obtained from the concentrated $MgSO_4$ solution varies with the amount of added NH_4OH. As the amount of added NH_4OH was decreased, the ratio of the plate-like $Mg(OH)_2$ decreased, and the ratio of the needle-like 513 MHSH increased. When 70 ml of 4M NH_4OH was added, single-phase $Mg(OH)_2$ was synthesized. The presence of plate-like aggregated materials was confirmed by SEM (Fig. 3e). When 50 mL of 4M NH_4 OH was added, $Mg(OH)_2$ and 513 MHSH existed in a mixed state (Fig. 3d). When 46 ml of NH_4OH was added, 513 MHSH with a needle-like structure with a diameter of 0.5-1.5 µm and a length of 15-20 µm was observed (Fig. 3c). The pH of the reaction solution significantly affects the dissolution equilibrium of $Mg(OH)_2$ and controls the concentrations of Mg^{2+} and $MgOH^+$ ions in the solution [20, 21]. When 46, 50, and 70 ml of NH_4OH were added, the pH of the solution remained constant at 10. The Mg^{2+}/OH^- ratio was controlled without changing the pH by Le Chatelier's principle because a weak base was used. When a strong base solution is used, $Mg(OH)_2$ is generated preferentially, which makes it challenging to obtain high-purity 513 MHSH.

Synthesis of $Mg(OH)_2$ from the sea bittern

$Mg(OH)_2$ was synthesized by adding ammonia to the $MgSO_4$ from the sea bittern at room temperature. The OH^- ions combine with Mg^{2+} ions in the solution, precipitating as $Mg(OH)_2$. Fig. 4 shows the XRD pattern (Fig. 4a) and TEM image (Fig. 4b) of the $Mg(OH)_2$ from the sea bittern. Adding 2 M NaOH resulted in the formation of $Mg(OH)_2$, confirmed as plate-like particles roughly 50-70 nm in size.

$Mg(OH)_2$ particle growth in a basic condition through hydrothermal treatment

$Mg(OH)_2$ obtained by adding a basic precipitant to sea

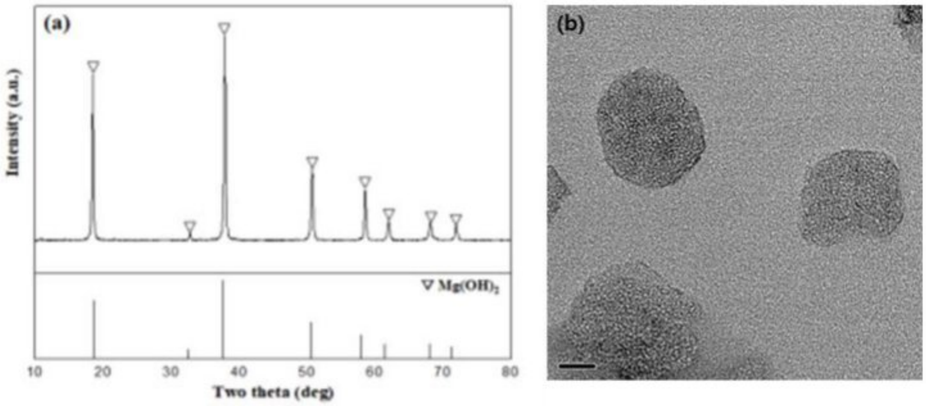

Fig. 4. (a) XRD pattern of the products synthesized with sea bittern, (b) TEM image of $Mg(OH)_2$ obtained from sea bittern.

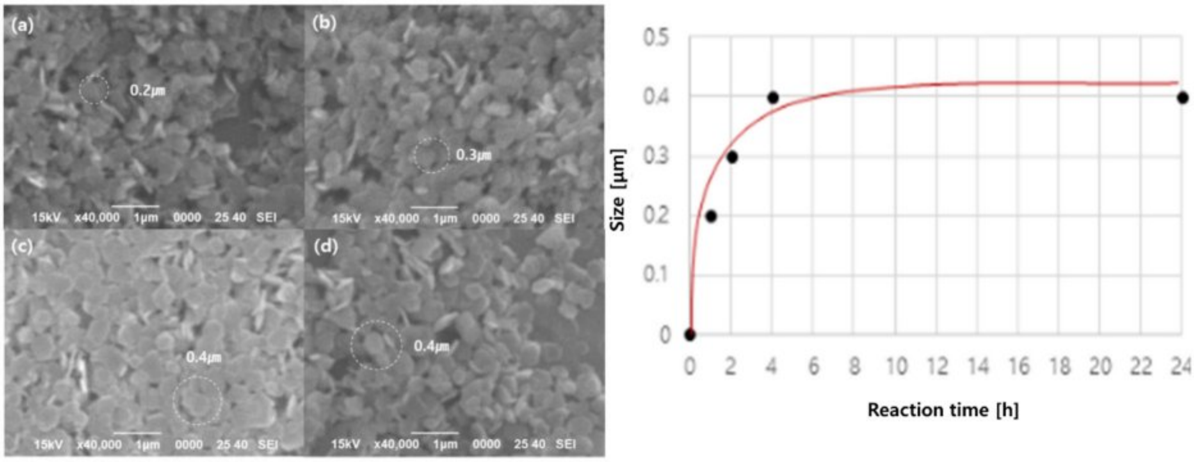

Fig. 5. SEM images of the $Mg(OH)_2$ after hydrothermal treatment in 2 M NaOH 180 °C at different reaction time: (a) 1 h, (b) 2 h, (c) 4 h, (d) 24 h, (e) the data of particle size growth according to the hydrothermal reaction time.

bittern was dispersed in a 2 M ammonia solution, and the size of the $Mg(OH)_2$ particles was increased through a hydrothermal reaction at 180 °C. Fig. 5 shows the SEM images and data showing the change in the size of the $Mg(OH)_2$ particles according to the hydrothermal reaction time. It was confirmed that the particle size of $Mg(OH)_2$ (50 nm) increased as the hydrothermal reaction time was extended (Fig. 5a, 5b, 5c). However, the particle size reached approximately 400 nm after 4 hours of hydrothermal treatment and showed no significant growth beyond that point (Fig. 5d). Fig. 5e shows the trend in the $Mg(OH)_2$ particle size change over time. Therefore, it was found that the optimal hydrothermal reaction condition for growing the particles of $Mg(OH)_2$ was a reaction at 180 °C for 4 hours.

This result was also observed when magnesium hydroxide was synthesized by excessive addition of NH_4OH during 513 MHSH synthesis. This result is because $MgOH^+$ was precipitated around the initial $Mg(OH)_2$ particles and grew as hexagonal plate-like particles as the dissolution and re-precipitation process occurred in the hydrothermal vessels. This result suggests that $Mg(OH)_2$ synthesis and particle growth can be achieved simultaneously [23].

Influence of H_2SO_4 (acid catalyst) on the formation of 513 MHSH whiskers

Figure 6 and 7 present the XRD patterns and SEM images of the products obtained using H_2SO_4 and the $Mg(OH)_2$ derived from the sea bittern. As shown in Fig. 6, an increase in the amount of H_2SO_4 reacting with the $Mg(OH)_2$ solution led to a decrease in the XRD peak of $Mg(OH)_2$. Specifically, when 30 mL of a 5M H_2SO_4 solution was added, predominantly needle-like 513 MHSH structures were observed (Fig. 6a). The addition of 10 and 20 mL of the 5M H_2SO_4 solution resulted in a mixture of $Mg(OH)_2$ and 513 MHSH (Fig. 6b and 6c). The pH decreased within the weak alkaline range from pH 8 to 10 as the H_2SO_4 concentration was increased, leading to the disappearance of $Mg(OH)_2$ and the formation of pure 513 MHSH. This phenomenon occurs because the solubility of $Mg(OH)_2$ increases as the pH decreases [29]. Consequently, it can be inferred that an increased amount of H_2SO_4 results in higher concentrations of Mg^{2+} and $MgOH^+$ due to the dissolution of $Mg(OH)_2$, thereby facilitating the formation of 513 MHSH [18, 19].

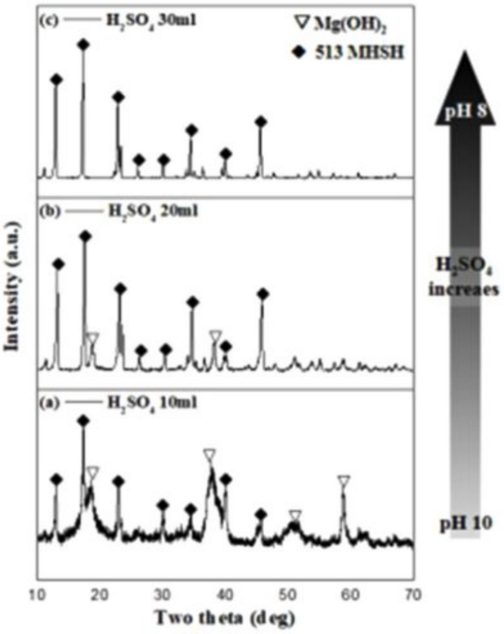

Fig. 6. XRD patterns of the products synthesized with 4 M $Mg(OH)_2$ and varying volumes of H_2SO_4 solution: (a) 30 ml, (b) 20 ml, (c) 10 ml

$$Mg(OH)_2 \leftrightarrow Mg(OH)^+ + OH^-$$

$$Mg(OH)^+ \leftrightarrow Mg^{2+} + 2OH^-$$

$$Mg(OH)_2 + 4OH^- \leftrightarrow Mg(OH)_6^{4-}$$

$$6Mg(OH)_6^{4-} + SO_4^{2-} + 3H_2O \rightarrow 5Mg(OH)_2 \cdot MgSO_4 \cdot 3H_2O + 26OH^-$$

SEM confirmed these results. Fig. 7 shows that the ratio of needle-like 513 MHSH increased when more H_2SO_4 was added to the $Mg(OH)_2$. In Fig. 7b and 7c, the hexagonal plate-like $Mg(OH)_2$ is dominant, while Fig. 7a shows only the needle-like 513 MHSH.

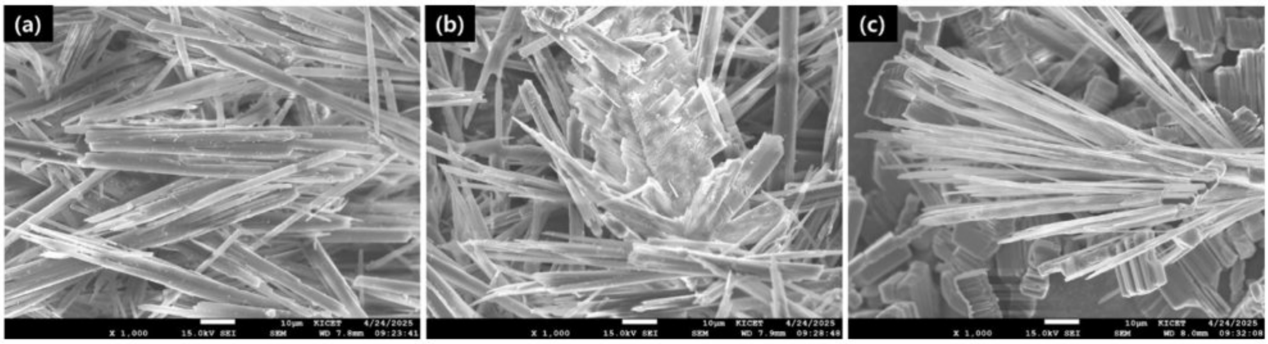

Fig. 7. SEM images of the products synthesized with 4 M $Mg(OH)_2$ and varying volumes of H_2SO_4 solution: (a) 30 ml, (b) 20 ml, (c) 10 ml

Conclusion

This study controlled the shape and size of $Mg(OH)_2$ and 513 MHSH by efficiently extracting $MgSO_4$ from sea bittern and controlling the amount of ammonia. The $MgSO_4$ solution obtained by precipitating Ca^{2+} as $CaSO_4$ through the addition of sulfuric acid to sea bittern is an important raw material for synthesizing needle-like 513 MHSH. Because the Mg concentration of sea bittern is generally lower than the Mg^{2+} ion concentration required for synthesis, needle-like 513 MHSH can be synthesized by controlling the Mg content and the amount of ammonia. In addition, ammonia or NaOH, which is a basic precipitant, is added to obtain $Mg(OH)_2$ as hexagonal plate-like particles 50 nm in size, which can be grown to 400 nm through a hydrothermal reaction. In addition, sulfuric acid can be added to the hexagonal plate-like $Mg(OH)_2$ to synthesize the needle-like 513 MHSH through a hydrothermal reaction. In this study, Ca^{2+} ions present in sea bittern were effectively removed using sulfuric acid. $MgSO_4$ was synthesized and, with the use of a basic catalyst, used to produce both needle-like 513 MHSH and hexagonal plate-like $Mg(OH)_2$. Additionally, sulfuric acid was added to $Mg(OH)_2$ to adjust the $Mg(OH)_2$ to $MgSO_4$ ratio, enabling the formation of the needle-like 513 MHSH. In this study, 513 MHSH was successfully synthesized by controlling the pH through the direct addition of precipitants to the solution without requiring purification or drying of the $MgSO_4$ raw material derived from sea bittern. Furthermore, 513 MHSH can be synthesized by exploiting the reversible conversion between $MgSO_4$ and $Mg(OH)_2$, using basic/acidic catalysts, both of which can be derived from sea bittern. This approach highlights the potential for domestic production of high-value-added compounds from low-cost resources through appropriate technological development.

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Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data used in this study are available upon reasonable request. Interested parties can contact the corresponding author to obtain the data. The data will be shared in a format that is suitable for further analysis, subject to any applicable data use agreements or ethical constraints.

References

1. H. Lu, Y. Hu, L. Yang, J. Xiao, Z.Wang, Z. Chen, and W. Fan, Macromol. Mater. Eng. 289[11] (2004) 984-989.
2. H. Lu, Y. Hu, L. Yang, Z. Wang, Z. Chen, and W. Fan, J. Mater. Sci. 41 (2006) 363-367.
3. A. Choi, N. Oh, and Y. Kim, J. Korean Ceram. Soc. 59 (2022) 224-228.
4. Y. Tanga and X. Yuea, J. Ceram. Process. Res. 26[2] (2025), 299-306.
5. C. Gao, X. Li, L. Feng, Z. Xiang, and D. Zhang, Chem. Eng. J. 150[2-3] (2009) 551-554.
6. X. Ning, C. Wu, and H. Chen, Materials 15[22] (2022) 8018.
7. K. Kang and D. Lee, J. Ind. Eng. Chem. 20[4] (2014) 2580-2583.
8. Y. Tao, G. Shiyang, Z. Lixia, X. Shiuping, and Y. Kaibei, J. Mol. Struct. 616[1-3] (2002) 247-252.
9. E. Kim, Y. Kim, and J. Nam, J. Mater. 4[2] (2018) 149-156.
10. H. Iwanaga, M. Kawaguchi, and S. Motojima, Jpn. J. Appl. Phys. 32 (1992) 105.
11. J. Park, S. Kang, and W. Kim, J. Ceram. Process. Res. 10[3] (2009) 364-366.
12. H. Guo and D. H. Yoon, J. Ceram. Process. Res. 6[4] (2005) 321-325.
13. H.M. Lim and J. Yun, J. Ceram. Process. Res. 10[4] (2009) 571-576.
14. R.S. Plentz, M. Miotto, E.E. Schneider, M.C. Forte, R.S. Mauler, and S.M.B. Nachtigall, J. Appl. Polym. Sci. 101[3] (2006) 1799-1805.
15. H. Gui, X. Zhang, W. Dong, Q. Wang, J. Gao, Z. Song, J. Lai, Y. Liu, and F. Huang, Polymer 48[9] (2007) 2537-2541.
16. L. Qiu, R. Xie, P. Ding, and B. Qu, Compos. Struct. 62[3-4] (2003) 391-395.
17. J. Lv, L. Qiu, and B. Qu, J. Cryst. Growth 267[3-4] (2004) 676-684.
18. X. Yan, D. Xu, and D. Xue, Acta Mater. 55[17] (2007) 5747-5757.
19. X. Sun, W. Shi, L. Xiang, and W. Zhu, Nanoscale Res. Lett. 3 (2008) 386.
20. R. Yu, J.H. Pee, H.T. Kim, K.J. Kim, Y.W. Kim, and Y.J. Kim, Key Eng. Mater. 512 (2012) 91-94.
21. R. Yu, J.H. Pee, H.T. Kim, K.J. Kim, Y.W. Kim, W. Kim, and Y.J. Kim, J. Korean Powder Metall. Inst. 18[3] (2011) 283-289.
22. R. Yu, J.H. Pee, H.T. Kim, and Y. Kim, J. Korean Ceram. Soc. 50[3] (2013) 201.
23. R. Yu and Y. Kim, J. Korean Powder Metall. Inst. 26[3] (2019) 195-200.
24. M. Park, A. Choi, S. Kim, W. Shim, and Y. Kim, J. Korean Ceram. Soc. 59 (2022) 869-875.
25. H. Shim, J. Kim, A. Choi, N. Oh, and Y. Kim, J. Korean Powder Metall. Inst. 32[2] (2025) 122-130.
26. J. Chen, L. Lin, Y. Song, and L. Shao, J. Cryst. Growth 311[8] (2009) 2405-2408.
27. C. Henrist, J.P. Mathieu, C. Vogels, A. Rulmont, and R. Cloots, J. Cryst. Growth 249[1-2] (2003) 321-330.
28. Y. Zhang, Z. Yang, D. Guo, H. Geng, and C. Dong, Procedia Environ. Sci. 18 (2013) 84-91.
29. H. Schott, J. Pharm. Sci. 70[5] (1981) 486-489.