

# Microwave Assisted Preparation of Magnesium Hydroxide Nano-sheets

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**Abstract** In this paper, we present a novel synthesis approach for preparation of Magnesium Hydroxide, Mg(OH)<sub>2</sub>, having nano-sheets morphologies that can find applications in plastic industry as flame-retardant and reinforcing material and can be used for conservation of paper based cultural heritage. The nanomaterials were successfully synthesized using novel microwave synthesis technique using Magnesium sulfates as precursor and Cetyltrimethylammonium bromide (CTAB) as dispersant. The nano-sheets were produced through a reaction of Magnesium sulfates with NaOH in a microwave chemical reactor, operated at a controlled power rating for specific time. A good yield of the precipitates, produced as a result of reaction, were isolated, washed, dried and were subjected to heat treatment at 300°C to remove the organic dispersant. Characterization technique such as XRD, SEM, HR-TEM were used to elucidate the composition and structure of Mg(OH)<sub>2</sub> nanomaterial. The data obtained from these techniques confirmed successful synthesis and nano-structure of Mg(OH)<sub>2</sub>. The BET surface area and nitrogen adsorption/desorption measurements of Mg(OH)<sub>2</sub> nanoparticles showed a surface area of 80.27 m<sup>2</sup>/g. HRTEM analysis revealed the morphology of Mg(OH)<sub>2</sub> to be composed of nano sheets with a unique packing structure that gives a highly porous nano structure to the material. The Mg(OH)<sub>2</sub> particles with a size smaller than 5 nm were observed which, in our opinion, can be used for diverse applications.

**Keywords:** Magnesium Hydroxide, Nano-sheets, Microwave-Assisted synthesis, CTAB, Magnesium Sulfate

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## 1. Introduction

Magnesium hydroxide (Mg(OH)<sub>2</sub>) is used for diverse applications such as to neutralize acidic waste streams and gases rich in sulfuric oxides [1], as antacid excipient in pharmaceuticals [2], in pulp and paper industry as acidic waste neutralizer, in environment protection and paper making industry [1,2] and as fertilizer additive. Besides, it has also been used as the most important precursor for the preparation of magnesium oxide [3,4], as flame-retardant filler [5,6,7,8] and as reinforcing material in polymer composites [9,10].

Magnesium hydroxide can be prepared by several methods, such as hydration of magnesium oxide [4], sol-gel techniques [11], electrolysis of magnesium salt aqueous solutions, and precipitation. No matter what it is used for, its morphology and particle size play important roles on its usages. Mg(OH)<sub>2</sub> can have lamellar, rod or needle like structure or morphologies. The magnesium cation being six-fold coordinated by hydroxyl groups results in Mg(OH)<sub>6</sub> octahedron [12]. Such a layered crystal structure is an advantage for lamellar crystal of the compound. The common precipitation method can only

produce lamellar Mg(OH)<sub>2</sub> [10]. To prepare special morphological Mg(OH)<sub>2</sub>, novel methods should be used, such as hydrothermal or solvo-thermal technique for rod-like [13,14,15,16], tube-like [14], needle-like [14,15], lamella-like [14,15,17,18,19] and bone-like [20] Mg(OH)<sub>2</sub>; liquid-solid arc discharge technique [21] for nano-rods, pulsed-laser-induced reaction [22] for needle-like whereas microwave-assisted synthesis method [23] for fiber-like Mg(OH)<sub>2</sub>. The nano-particles of Mg(OH)<sub>2</sub> with controlled size, shape, and structure (rods and tubes) can be synthesized by hydrothermal technique [10,13]. Nanosized Mg(OH)<sub>2</sub> is prepared by employing pulsed laser ablation technique where a Mg plate immersed in deionized water, is ablated [22]. The plate-shape nano-Mg(OH)<sub>2</sub> powder can be prepared through the calcination of magnesite tailings [24]. Magnesium hydroxide with plate-like crystalline structure, is prepared by flash precipitation, using MgF<sub>2</sub>, MgCl<sub>2</sub>, MgBr<sub>2</sub>, MgI<sub>2</sub>, MgBrO<sub>3</sub>, MgSO<sub>4</sub>, and MgClO<sub>3</sub> and by employing Ultrasonic mixing [25]. Fiber-like Mg(OH)<sub>2</sub> nanoparticles are synthesized by precipitation of magnesium nitrate with an alkaline solution, employing microwave irradiation as assistance [26]. Magnesium hydroxide with BET lower than 10 m<sup>2</sup>/g and average particle size between 0.5 and 10 μm can be synthesized by precipitating aqueous solution of magnesium chloride

with an excess of ammonia followed by hydrothermal recrystallization [27].  $\text{Mg}(\text{OH})_2$  obtained from sea water or brine, is etched in a solution of organic or inorganic acid to reduce average surface area [28].

However, all these physical or chemical synthesis methods have inherent problems such as low yields and impurities. As a result, it is still desired to develop a method capable of generating nanosized  $\text{Mg}(\text{OH})_2$  in a moderate quantity with a well-controlled dimension and morphology. In this regard, to the best of our knowledge, there are very few reports on the synthesis of  $\text{Mg}(\text{OH})_2$  with nano-sheet morphologies directly obtained from wet precipitation, though some reports suggest preparation of layered double hydroxides (LDHs) by this method with some kinds of cations [29,30].

The novelty of our work is the use of magnesium sulfate solution along with CTAB in a microwave-assisted synthesis of magnesium hydroxide in the form of nano-sheets having a BET surface area of  $>80 \text{ m}^2/\text{g}$ . The yield of this method is significantly high in comparison with other reported method.

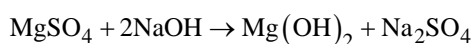
## 2. Experimental

### 2.1. Materials

All chemicals are reagent grade and used without further purification. The chemicals, like Magnesium Sulfates ( $\text{MgSO}_4$ , medical Grade, Bell, sons &, UK: Labchem, 99%), Sodium Hydroxide ( $\text{NaOH}$ , Sigma Aldrich) and Cetyltrimethylammonium bromide (CTAB, Sigma Aldrich, 99%) were used as received without further purification. Distilled water and pure ethanol were used in all the preparation.

### 2.2. Microwave Assisted Preparation of Nanoparticles

Microwave irradiation method was used for synthesis of extremely small sized (5-10 nm)  $\text{Mg}(\text{OH})_2$  nano-sheets. The method is based on the reduction of metal sulfate using  $\text{NaOH}$  as reducing agent in a microwave chemical reactor. During the synthesis process, power/exposure of microwave radiations to the reactants was optimized along with pH of the solution with  $\text{NaOH}$  content. The  $\text{Mg}(\text{OH})_2$  nano-sheet samples were obtained by wet homogeneous precipitation in the presence of dispersant CTAB. The reaction proceeded as follows:



In this method,  $\text{MgSO}_4$  was used as a precursor,  $\text{NaOH}$  solution was used as precipitator. The dispersant or surfactant was used to prevent the products from aggregating.

In a typical synthesis process, a precursor solution is prepared by dissolving 5 g of Magnesium sulfates in 100 mL of DI water along with 1% solution of CTAB surfactant in a 250 ml reaction flask with addition of some alcohol. The contents are mixed at boiling temperature by stirring or sonication. The solution is kept stirring while 1M  $\text{NaOH}$  is being added drop-wise to it. The addition is continued until the solution is transformed into a white colored translucent form. The solution is subsequently

placed in a microwave chemical reactor (MCR-3), operated at a power of 266 W, for 10-15 minutes and is removed upon the onset of boiling. The content is allowed to cool down naturally to ambient temperature. Finally, the precipitated particles are filtered and collected after washing thoroughly several times with distilled water and ethanol. The dried powder samples are heated in oven at  $300^\circ\text{C}$  to remove the CTAB.

### 2.3. Characterization

Morphology and microstructure investigations were performed with scanning and transmission electron microscopes (SEM and TEM). Scanning electron microscopic images are obtained with a HITACHI SU-70 SEM with an accelerating voltage of 5 keV. High Resolution Transmission electron microscopy (HRTEM; model: JEOL JEM-2100F) was used for the morphological and crystallographic characterization of the nanoparticles. Phase identification was evaluated by X-ray diffraction (XRD) technique. X-ray diffraction of the nanoparticles were recorded by using a Rigaku MiniFlex600 ( $\text{CuK}\alpha$  radiation, wavelength =  $1.54 \text{ \AA}$ ) operated at 40 kV, 15 mA. The surface area of the nanoparticles was measured using BET Surface Area Analyzer through nitrogen adsorption/desorption measurements carried out at 77 K (Quanta chrome Instruments, Nova 2200e).

## 3. Results and Discussion

Figure 1 shows X-Ray Diffraction pattern of  $\text{Mg}(\text{OH})_2$  Nanoparticles synthesized in this study. The XRD patterns are consistent with the X-ray diffraction pattern of crystalline  $\text{Mg}(\text{OH})_2$  Nanoparticles. The XRD pattern of  $\text{Mg}(\text{OH})_2$  which was verified using the JCPDS card no. 00-007-0239, shows a broad peaks with high intensities of  $\text{Mg}(\text{OH})_2$  crystallites with a maximum peak from (101) crystal plane at 2 Theta of 38.017 degrees. The broadening of the peaks indicates that the particles are small which was further confirmed by HRTEM analysis (Figure 3). Thus the data reported in Figure 1 and discussed above, suggests successful preparation of the desired materials.

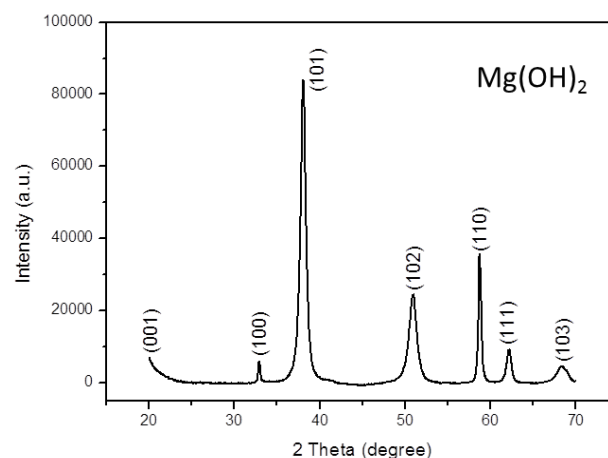
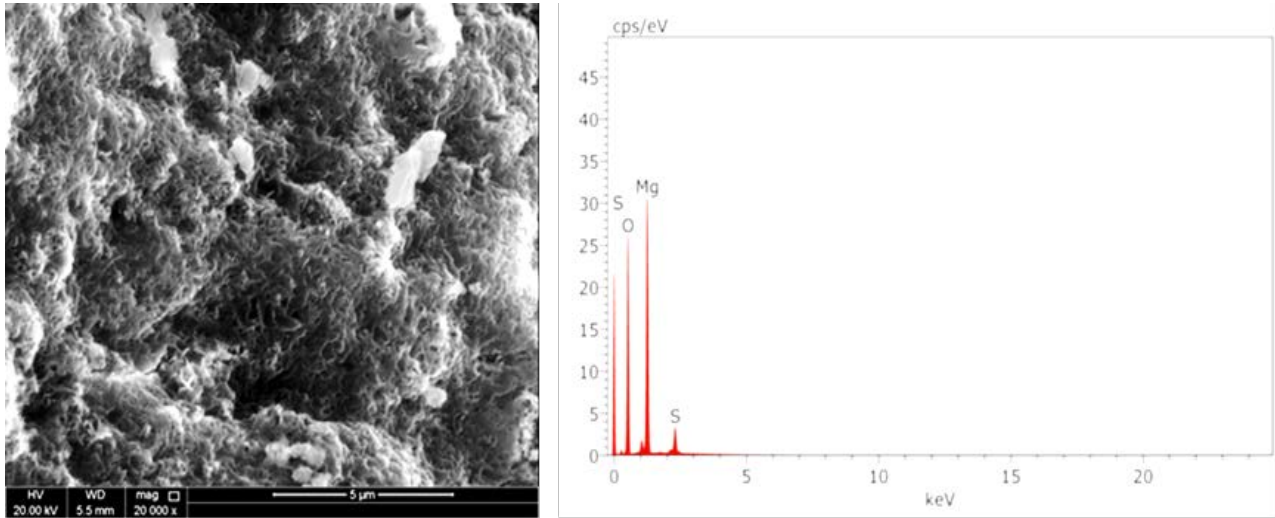


Figure 1. XRD patterns of  $\text{Mg}(\text{OH})_2$  Nanoparticles.

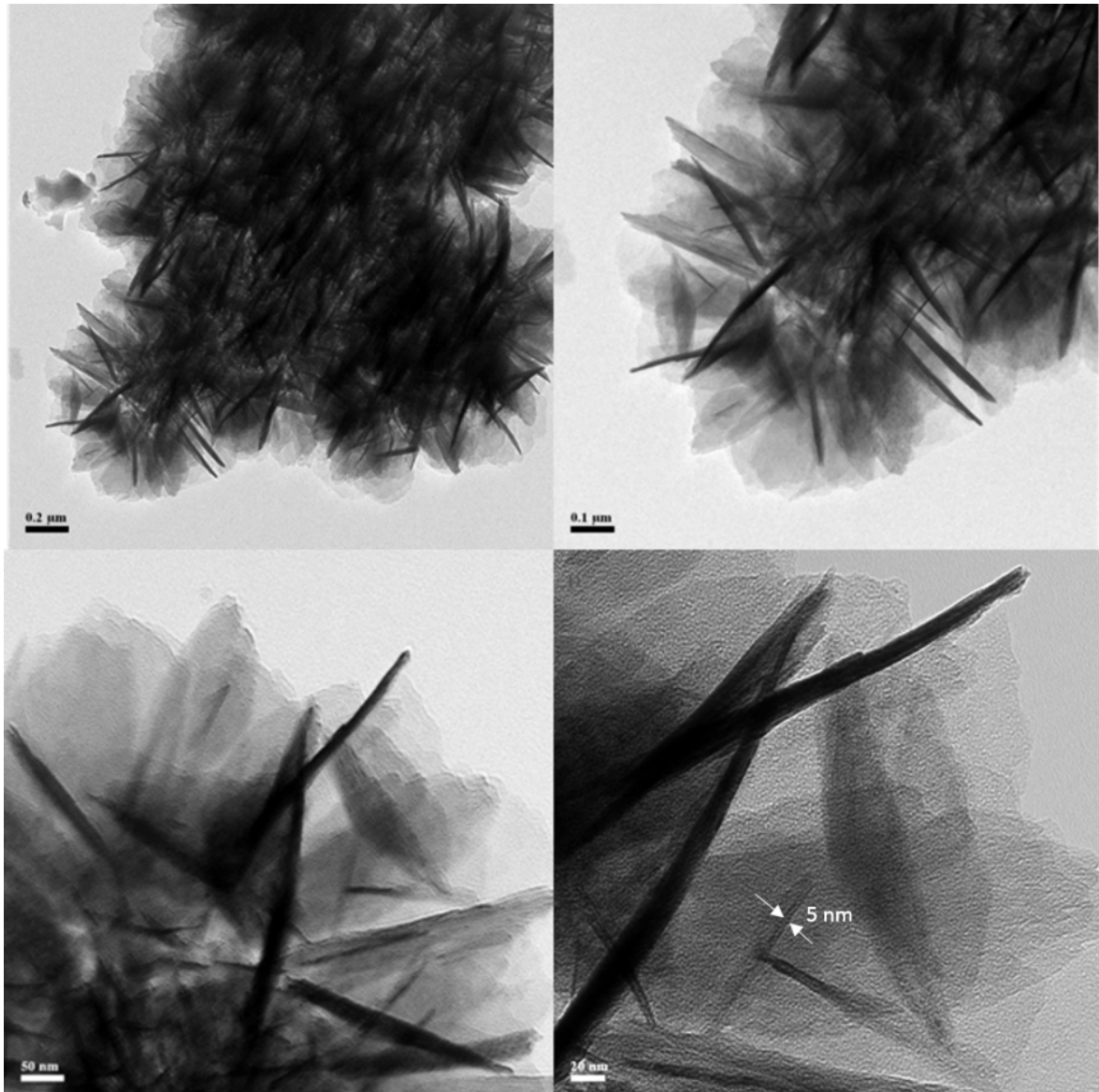
Figure 2 shows micrograph of Scanning Electron Microscope (SEM) and Energy Dispersed X-Ray (SEM-EDX) spectra obtained for  $\text{Mg}(\text{OH})_2$  Nanoparticles synthesized in this study. It is evident that the structure of

$\text{Mg}(\text{OH})_2$  is highly porous with small particle size ( $\lesssim 20$  nm). The analysis revealed that element distributions maps of the elements are mostly consist of Magnesium and oxygen which is consistent with element present in this

material. However, there are some sulfur peaks present which is related to the tape used as a sample holder or may be from the unreacted  $\text{MgSO}_4$ .



**Figure 2.** Scanning electron micrograph (SEM) and SEM-EDX spectra with the distribution of elements obtained of  $\text{Mg}(\text{OH})_2$  nano sheets



**Figure 3.** High Resolution Transmission electron microscopy (HRTEM) micrograph of  $\text{Mg}(\text{OH})_2$  Nano Sheets at different magnifications

Figure 3 shows the High Resolution Transmission electron microscopy (HRTEM) micrograph of Mg(OH)<sub>2</sub> nano sheets. The morphology of Mg(OH)<sub>2</sub> nano sheets has a unique structure of highly porous nano sheets consisting of small particles with a size of smaller than 5 nm.

The specific surface area of a powder is estimated from the amount of nitrogen adsorbed in relationship with its pressure, at the boiling temperature of liquid nitrogen under normal atmospheric pressure. The observations are interpreted following the model of Brunauer, Emmett and Teller (BET Method). The BET equation

$$\frac{1}{v[(p_0/p)-1]} = \frac{c-1}{v_m c} \left( \frac{p}{p_0} \right) + \frac{1}{v_m c}$$

where  $p$  and  $p_0$  are the equilibrium and the saturation pressure of adsorbates at the temperature of adsorption,  $v$  is the adsorbed gas quantity, and  $v_m$  is the monolayer adsorbed gas quantity. The  $c$  is the BET constant,

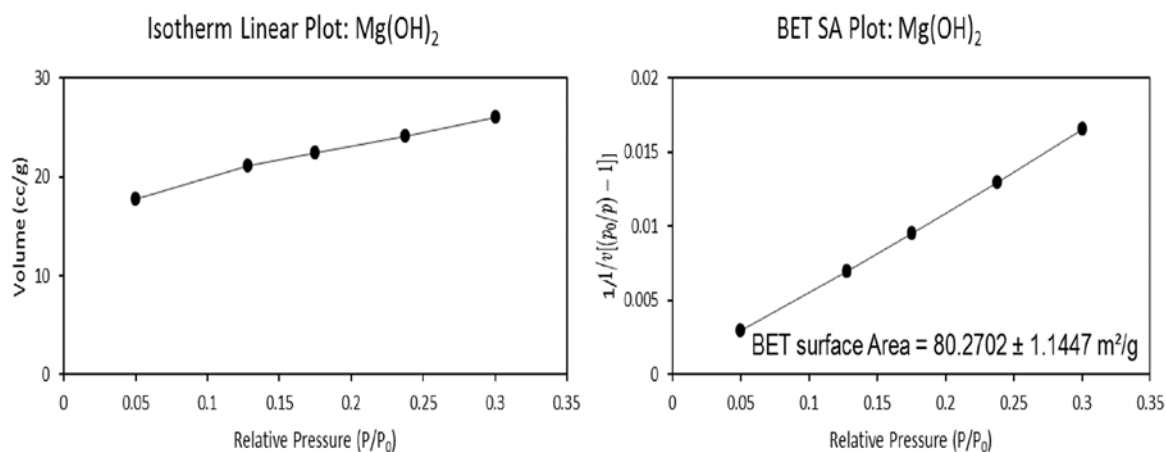


Figure 4. BET Surface Area and nitrogen adsorption/desorption measurements of Mg(OH)<sub>2</sub> Nano Sheets synthesized in this study

The full optimization of the synthesis and the characterization Mg(OH)<sub>2</sub> nano sheets is a continuing task and we are currently exploring the mechanical properties of this material and the potential usage in different applications such as thin films, paper manufacturing, packaging, and construction industry.

## 4. Conclusions

The study was aimed at preparation of nano-sheets of MH for various applications including conservation of paper based cultural heritage and flame-retardant and reinforcing material for plastic industry. The nanomaterials were successfully synthesized using novel microwave synthesis technique. Characterization technique such as XRD, SEM, HRTEM were used to elucidate the composition and structure of Mg(OH)<sub>2</sub> nanomaterials. The data obtained from these techniques confirmed successful synthesis and nano-structure of Mg(OH)<sub>2</sub>. The BET Surface Area and nitrogen adsorption/desorption measurements of Mg(OH)<sub>2</sub> nanoparticles showed a surface area of 80.27 m<sup>2</sup>/g. HR-TEM analysis revealed the morphology of Mg(OH)<sub>2</sub> to be composed of nano sheets with a unique packing structure that gives a highly porous nano structure to the material. The Mg(OH)<sub>2</sub> particles with a size smaller than 5 nm have been observed.

$$c = \exp\left(\frac{E_1 - E_L}{RT}\right)$$

where  $E_1$  is the heat of adsorption for the first layer, and  $E_L$  is that for the second and higher layers and is equal to the heat of liquefaction. Using BET equation, an adsorption isotherm has been plotted as a straight line with  $1/v[(p_0/p)-1]$  on the y-axis and  $p/p_0$  on the x-axis according to experimental results.

The BET surface area and nitrogen adsorption/desorption measurements for Mg(OH)<sub>2</sub> nanoparticles was measured using Quanta chrome Instruments, Nova 2200e. The data, depicted in Figure 4, shows that the surface area of Mg(OH)<sub>2</sub> sample is 80.27 m<sup>2</sup>/g. These results show that the high porosity and the high surface area of Mg(OH)<sub>2</sub> will impact the dispersion and the efficiency of Mg(OH)<sub>2</sub> as potential solution in the deacidification of cultural heritage papers and also as flame-retardant and reinforcing material in the plastic composite industries.

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