Synthesis of hierarchical structured MgO by sol-gel method

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ABSTRACT: Magnesium oxide (MgO) was synthesized by ultrasound assisted sol-gel method. The synthesized samples were characterized by various analytical techniques including X-Ray diffraction (XRD), field emission scanning electron microscopy (FESEM), SEM with (energy dispersive X-ray analysis) EDX, Fourier transform infrared spectroscopy (FTIR). SEM with EDX and XRD characterization studies confirmed that MgO particles thus obtained have hierarchical structures with high purity, and the particle sizes vary within the range of 30 nm to several µm. The particles are uniformly spherical in shape. The elements presented in the sample were found by EDX. FTIR analysis confirmed the presence of Mg-O stretching in the sample. © Global Scientific Publishers 2013

KEYWORDS: XRD; FESEM; EDX; FTIR; hierarchical (micro & nano); sol-gel.

1. Introduction

During the last few years, synthesis of nanostructured metal oxide materials has attracted the researchers due to its potential applications [1]. Discoveries in the past decade reveals that the materials prepared in the form of very small particles change significantly in their physical and chemical properties, sometimes to the extent that a completely new phenomenon is established [2]. In recent years, researchers have focused more on the synthesis of MgO nanoparticles due to its novel applications in advanced technologies [3]. Metal oxides are extremely important technological materials to be used in electronic and photonic devices [4]. The magnesium oxide (MgO) is a very suitable candidate for insulation applications due to its low heat capacity and high melting point [5]. Recently, it has been reported that MgO has a good bactericidal performance in aqueous environments due to the formation of super-oxide [6]. Magnesium hydroxide is a non-toxic, non-corrosive, thermally stable, and environment-friendly, flame retardant, undergoing endothermic dehydration and suppressing fumes under fire conditions. Various kinds of fabrication techniques are employed to synthesize MgO nanoparticles such as chemical vapour deposition(CVD) [7], plasma enhanced chemical vapour deposition (PECVD) [8], pulsed laser deposition(PLD) [9], laser ablation [10], molecular beam epitaxy (MBE) sputtering method [11], hydrothermal method [12], sol-gel method [12,13], co-precipitation method [14] and thermal decomposition of hydroxide or carbonate [15, 16]. Among the above techniques, sol-gel process has become a promising option for the synthesis and large scale production of MgO nanoparticles [9]. New and inexpensive method to produce nano-sized MgO with narrow size distribution and larger surface area is necessary to solve certain problems like low reactivity and catalytic action. The sol–gel synthesis, followed by supercritical drying, spray pyrolysis and modified-citrate precursor technique, has been successfully applied to prepare high surface area MgO powders. Moreover the oxide morphology and the particle size depend on the preparation conditions like pH, gelling agent, calcination rate and temperature [17]. The ultrasonic waves can produce nano-sized metal oxides [18].

Previous studies [19] indicated that such extreme chemical and physical environment were helpful to increase the rate of synthetic reactions and to obtain smaller crystals with more uniform size distribution compared to the conventional techniques for synthesizing the nanoscale MgO.

The objective of the study is to synthesize hierarchically structured MgO particle with large surface area in a short reaction time at room temperature. It is the simplest, cost effective and ecofriendly method. The need of hierarchical structured MgO has higher catalytic activity than that of bulk MgO at lower temperature, due to its large surface area.

2. Experimental method

2.1 Reagents

Magnesium nitrate, $Mg(NO_3)_2.6H_2O$ (SPECTRUM, India), Sodium hydroxide, NaOH (HIMEDIA, India), Ammonia solution (HIMEDIA), Doubly distilled (DD) water were used for synthesis. The chemicals were employed without further purification.

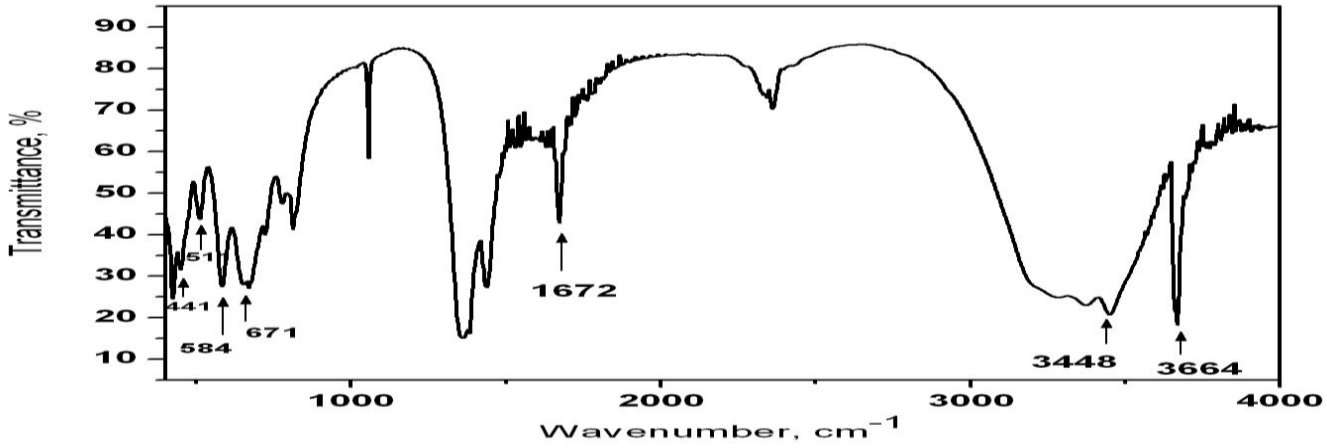

Figure 1. FTIR spectrum of magnesia nanoparticles.

2.2 Procedure

0.2 M Magnesium nitrate was dissolved in 100 mL of DD water and taken in a 250 mL beaker. 0.4 M NaOH was added drop by drop under sonication. The molar ratio of metal ions to hydroxide ions was maintained as 1:2. The mixture was then ultrasonicated for 2 hours at room temperature to form magnesium hydroxide without any agglomeration.

$$Mg(NO_3)_2 + 2NaOH \rightarrow Mg(OH)_2 + 2NaNO_3 \quad (1)$$

The magnesium hydroxide precipitate formed was filtered by washing it with doubly distilled water. It was followed by the addition of ethanol and the obtained sample was dried at 110^{o}C for 24 hours. Calcination was carried out at the temperature of 500^{o}C for 4 hours to obtain the purest form of MgO with hierarchical structure.

$$Mg(OH)_2 \rightarrow MgO + H_2O \quad (2)$$

Instead of NaOH, NH_4OH was taken as an agent. The same method was adopted for preparing MgO particles using NH_4OH.

$$Mg(NO_3)_2 + 2NH_4OH \rightarrow Mg(OH)_2 + 2NH_4NO_3 \quad (3)$$

$$Mg(OH)_2 \rightarrow MgO + H_2O \quad (4)$$

2.3. Characterization of material

The synthesized samples were characterized by the following analytical techniques, such as FTIR, FESEM, SEM and EDX. X-ray diffraction patterns of the prepared samples were obtained by Philips X'Pert PRO diffractometer equipped with an X'celerator detector, using nickel filtered CuKα radiation at λ = 1.541 Å. The measurements were taken at room temperature ranging of $10^o < 2\theta < 90^o$ using step scans. The step size and the scan rate were noted at 10^o per minute to determine the size of the crystallites. Surface morphology, elemental analysis and elemental mapping studies were carried out using a scanning electron microscope (SEM) operated at 4 kV equipped with energy dispersive analysis of X-rays (EDX) using Hitachi S-4500 SEM machine and FESEM was done by field emission scanning electron microscope model JSM- 670IF. FTIR was carried out with the range of 400 - 4000 cm^{-1} using IR Spectrophotometer Perkin-Elmer 783.

3. Results and discussion

3.1 FTIR analysis

FTIR Spectra of MgO particles are shown in Fig. 1. Peaks at 3664 cm^{-1}, 3448 cm^{-1} corresponding to the O–H stretching mode of hydroxyl groups were present on the surface due to moisture.

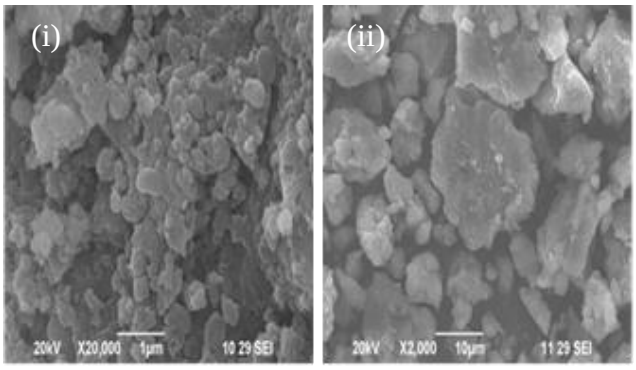

Figure 2. SEM image of MgO sample formed with (i) NaOH (ii) NH_4OH.

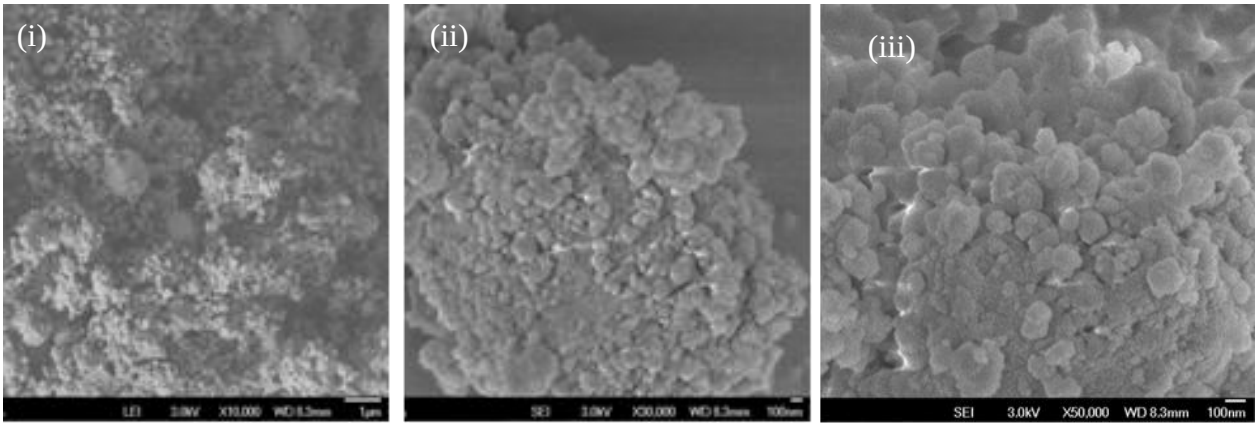

Figure 3. FESEM image of MgO sample for different magnification: (i) 10K (ii) 30K and (iii) 50K.

Peak at 1672 cm^{-1} was attributed to the bending vibration of water molecule. The major peaks at 449 cm^{-1}, 511 cm^{-1}, 584 cm^{-1}, 671 cm^{-1} which confirmed the presence of Mg-O vibrations [20, 21].

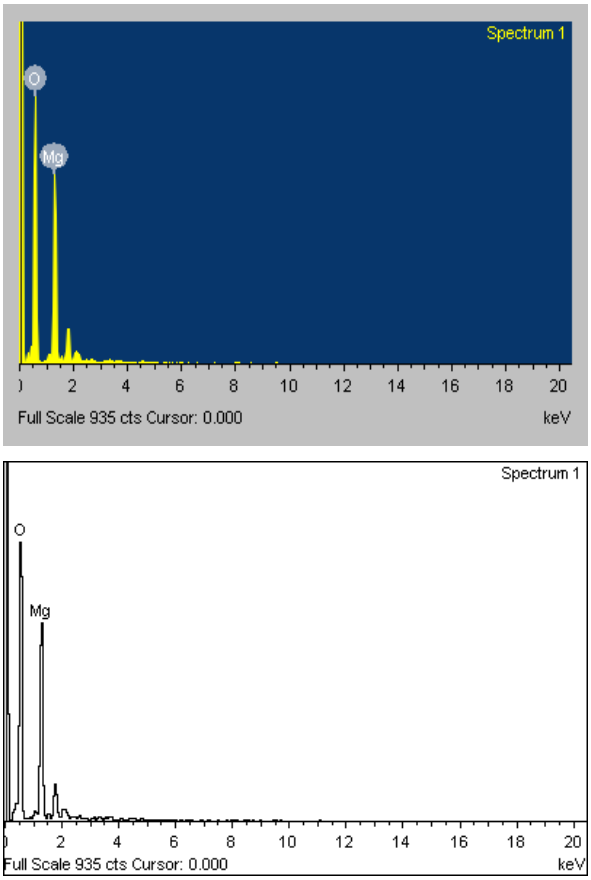

Figure 4. EDX spectrum of calcinated MgO nanoparticles.

3.2 SEM analysis

Fig. 2 shows the SEM images of MgO nanoparticles with NaOH and NH_4OH agent. The morphology, structure and size of the samples were investigated by SEM. It was observed that the average size of MgO particles using NaOH is smaller than the MgO using NH_4OH.

The average particle size calculated from the image is about 30-50 nm in the case of NaOH and is about 10 µm in the case NH_4OH. The size of the MgO particles calculated from SEM micrographs coincides well with those obtained using X-ray diffraction [22].

3.3 Field emission scanning electron microscopy analysis

FESEM was used to indicate the morphology and size distribution of the MgO nanoparticles. FESEM images of MgO nanoparticles with different magnification are shown in Fig. 3.

The average particle sizes of the prepared MgO sample fall ranging from 40 nm to several µm. Due to ultrasonication process, the particles are fine and spherical in shape. It is evident that FESEM results are in good agreement with the size distribution of MgO particles measured by XRD.

Table 1. Elemental ratio of MgO nanoparticles.

Element	Atomic %	Weight %
O	68.21	76.53
Mg	31.79	23.47
Total	100.0	100.0

3.4 EDX analysis

Energy dispersive X-ray spectroscopy (EDX or EDS) spectrum of the energy versus relative counts of the detected X-rays is obtained and evaluated for qualitative and quantitative determinations of the elements as shown in Fig. 4.

EDX reveals that the presence of Mg and O elements in MgO [20]. Graph demonstrates the typical EDX result of MgO. It is confirmed from the EDX analysis that the grown nanoparticles are composed of Mg and oxygen only. The molecular ratio of Mg:O of the MgO nanoparticles was found to be 1:2 (Table 1). No other peak for any other element can be found in the spectrum, which confirms again that the grown nanoparticles are pure MgO. In general, the ratios were fairly consistent with the molar ratios of the precursors used.

3.5 XRD analysis

The crystalline structure of nano MgO was determined by XRD analysis. Fig. 5 shows the (XRD) pattern of synthesized MgO nanoparticles. The existence of strong and sharp diffraction peaks located at the 2θ value of 37.1º, 43.1º, 62.5º corresponding to (1 1 1), (2 0 0) and (2 2 0) planes respectively indicated the formation of MgO [23]. The diffraction peaks of MgO can be matched with standard Joint Committee on Powder Diffraction Standards-JCPDS data [JCPDS file: 45-0946] [24].

The average particle size of the nanomaterial was determined using the following Debye - Scherrer equation and it was found to be 14.77 nm.

$$D = K\lambda/\beta\cos\theta \quad (5)$$

Where K is a constant equal to 0.89, β is the full width half maximum height of the diffraction peak at an angle θ and λ is wavelength. Table 2 indicates the average particle size of the MgO samples.

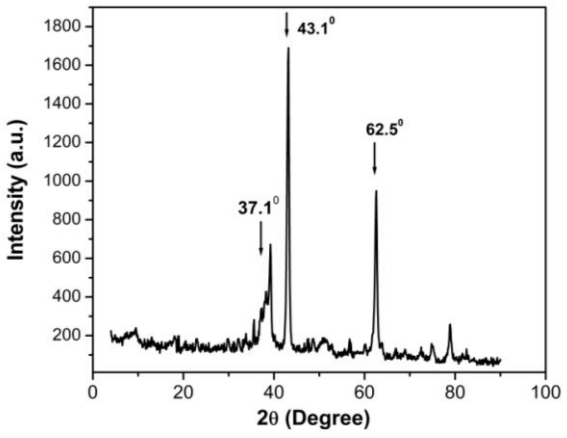

Figure 5. XRD pattern of MgO nanoparticles.

Table 2. Particle size determination from XRD data.

Obs. Max	Max Int. (a.u.)	FWHM (θ)	Particle size (nm)
37.1º	113	0.7112	11.66
43.1º	1016	0.5499	15.36
62.5º	575	0.5316	17.29

4. Conclusion

In the present work, hierarchically structured MgO was successfully synthesized by sol-gel method. The particles are nanometer in size when NaOH was used for the synthesis. In case of NH_4OH only micrometer particles were obtained. The formation of nanometer sized MgO particles was confirmed by XRD analysis. The results obtained from FESEM and SEM analysis showed that the particle size of MgO ranges from 30 nm to several μm with spherical shape. The presence of Mg and Oxygen in MgO was confirmed by EDX analysis.

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