

Synthesis of MgO nanoparticles using starch as precursor medium

Soo-Jong Kim* and Cheong-Hwa Han

Department of Advanced Materials & Chemical Engineering, Halla University, 28 Halladaegil, Wonju, Kangwon 26404, Korea

Nanocrystalline magnesium oxide (MgO) particles were prepared through liquid phase precursor (LPP) method using magnesium nitrate as starting material and starch as an impregnating matrix. The materials obtained by LPP method were subsequently annealed at 500–1,100 °C for 1–3 hrs to improve crystallinity and phase purity. Crystallization and the growth of particles were accelerated with increasing calcining temperature. Crystallization of MgO started around 500 °C, which the temperature is pyrolysis of starch, cubic phase generated at 600 °C. Moreover, above 600 °C, calcining time had influence on crystal growth. The obtained MgO nanoparticles were characterized by powder X-ray analysis (XRD), infrared (IR) spectroscopy, photoluminescence (PL), and field emission scanning electron microscopy (FE-SEM). The PL emission spectrum of MgO nanoparticles exhibits two emission peaks at 560 and 618 nm which are due to various structural defects. The cubic crystal structure with crystalline size of 30–150 nm, is obtained at the calcination temperature of 500–900 °C.

Key words: MgO, Nanoparticles, Starch, Impregnation.

Introduction

MgO is a crystal of a cubic structure forms, such as rock salt or sodium chloride which has the physical and chemical stable properties at high temperatures. Because of these characteristics has been used as refractory, semiconductors, insulators, agriculture, chemical, construction, health care, basic raw materials for various industries, including the environment [1]. In particular, MgO nanoparticles having a high specific surface area has been applied in various fields [2–3]. For example, studies have been reported for the adsorbent to degradation by the destruction of toxic chemicals in a high specific surface area [4]. And studies have been reported for the bactericidal performance due to the generation of peroxide ions in the surface of MgO nanoparticle [5–6]. MgO nanoparticles have been synthesized by various methods such as spray pyrolysis, precipitation method, sol-gel method, microwave heat treatment method [7–10]. In this study, we use the liquid phase precursor method to synthesize MgO nanoparticles. The magnesium nitrate aqueous solution was used as a starting material. It was used for starch as a matrix in order to impregnate the aqueous magnesium salt solution. The heat treatment temperature of the impregnation mixture was investigated with respect to how it affects the particle size and crystal structure of the synthesized MgO.

Experimental

First, dissolve the starting material $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in deionized water to prepare a mixed solution. Fig. 1 shows a schematic flow diagram of the MgO nanoparticles prepared by the impregnation method. 0.5 mol of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 120 ml of distilled water to prepare an aqueous metal salt solution. This solution was stirred for 1 hr at room temperature, and impregnated with starch used as a

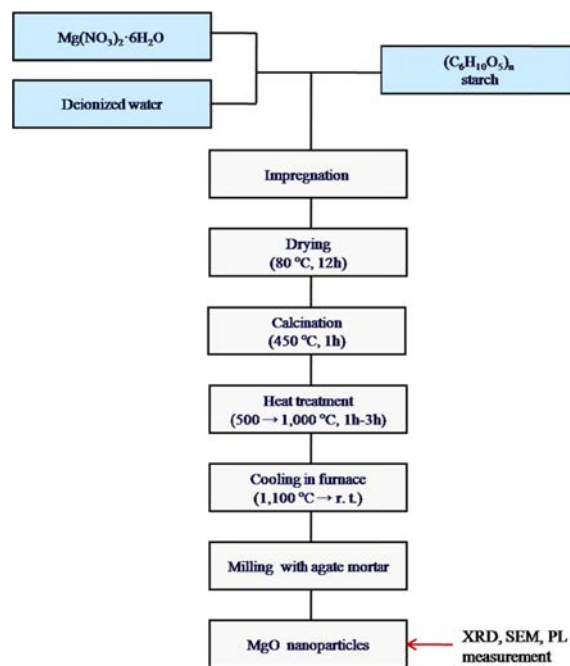


Fig. 1. Preparation procedures of MgO nanoparticles by liquid phase precursor method.

*Corresponding author:
Tel : +82-33-760-1237
Fax: +82-33-760-1290
E-mail: sjkim@halla.ac.kr

precursor matrix. Since starch, a natural polymer, has a higher density than a solution, its weight ratio to the solution is 1 : 1.2. The impregnated mixture was dried at 80 °C. for 24 h and calcined at 500 to 1,100 °C. for 3 hrs at a heating rate of 5 °C./min. The calcined samples were pulverized to obtain cubic MgO nanoparticles, and the characteristics of the synthesized samples were investigated by the following analytical method. To confirm the crystallinity of the calcined sample, an X-ray diffraction pattern was examined with a PAN alytical X-ray Diffractometer from X'Pert PRO MPD. A Cu Ka radiation and Ni filter was used. A scanning speed of 5 °/ min, a voltage of 40 kV, and a current of 30 mA in a diffraction angle (2 Θ) Range of 10 to 80 deg. The thermal analysis of the impregnated precursor were determined by differential scanning calorimeter (Scinco DSC N-650) and thermogravimetric analysis (TGA N-1000). The heating rate of the sample was 10 °C min, with a flowing N₂ atmosphere. The morphology of MgO nanoparticles at different temperatures were examined by FE-SEM (Model S-4300, Hitachi). For the comparative analysis of the particle size and the particle size distribution, the magnifications of all samples were uniformly measured at 10,000, 30,000, 50,000 and 100,000 times, respectively. Absorption and fluorescence spectra were observed using a fluorometer (FluoroMate FS-2, SCINCO) with a xenon lamp as the light source.

Result and Discussion

MgO nanoparticles having a uniform nanosized particle size distribution were prepared by using starch as an impregnating matrix. The microstructure of the starch used in the experiment is shown in Fig. 2. Starch is a natural polymer and has a micro fibril or micelle structure with a size of 1 μ m or less, so that the shape of particles produced depends on this structure. The starch particles shown in Fig. 2(a) are spherical particles of about 10 μ m in size before Mg(NO₃)₃·6H₂O is impregnated. Fig. 2(b) shows starch particles after impregnation, showing that the metal salt penetrates into the microstructure of starch and is uniformly impregnated. After the metal salt is impregnated, the size of the particles is slightly increased. By using starch with microstructure as a mediator, the aqueous solution containing the starting metal salt is uniformly impregnated in the microstructure of Starch. After the impregnated mixture was dried and heat-treated,

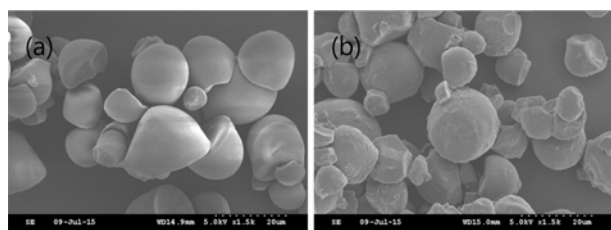


Fig. 2. FE-SEM images of (a) starch, and (b) impregnated starch.

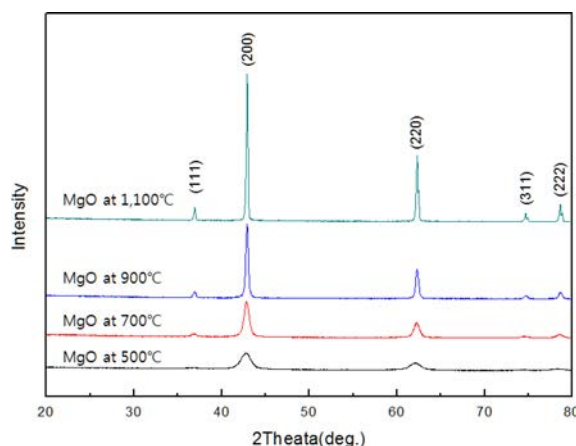


Fig. 3. XRD patterns of MgO nanoparticles heat treated at (a) 500 °C, (b) 700 °C, (c) 900 °C and (c) 1,100 °C.

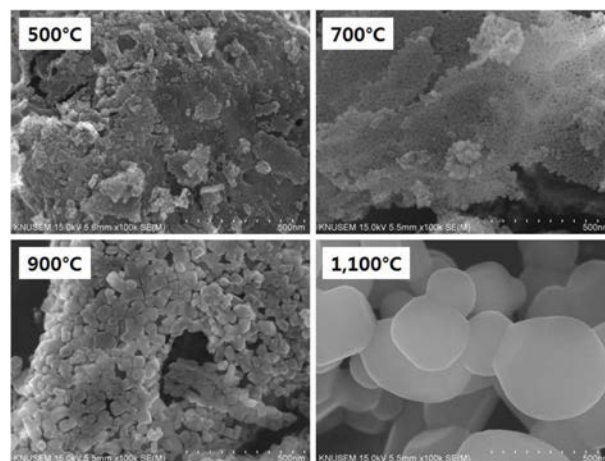


Fig. 4. FE-SEM images of MgO nanoparticles at various calcination temperatures, (a)500 °C, (b)700 °C, (c)900 °C, (d)1100 °C.

a nano-sized MgO powder having a uniform particle size could be produced. The results of X-ray diffraction analysis according to the heat treatment temperature (600 ~ 1,100 °C) of the prepared MgO particles are shown in Fig. 3. The diffraction peaks of MgO were distinct and the main peaks exhibiting high diffraction intensity were in good agreement with the standard JCPDS card (No. 45-0946). The XRD patterns of the annealed samples were analyzed and all the samples were found to have a cubic crystal structure. Peaks were shown at 37 °, 42 °, 62 °, 74 ° and 78 ° and their miller indices values correspond to (111), (200), (220), (311) and (222) respectively. Fig. 3(a), a crystal phase of MgO particles started to form at 500 °C. As the firing temperature increases from 600 °C to 1,100 °C, the intensity of the peak tends to increase and the crystallization progresses. Fig. 4 shows the results of FE-SEM measurement of the surface structure of the synthesized MgO particles when the heat treatment time was fixed to 3 hrs and the heat treatment temperature was changed from 600 to 1,100 °C. As shown in the XRD pattern of Fig. 3, already fine crystals are formed at a

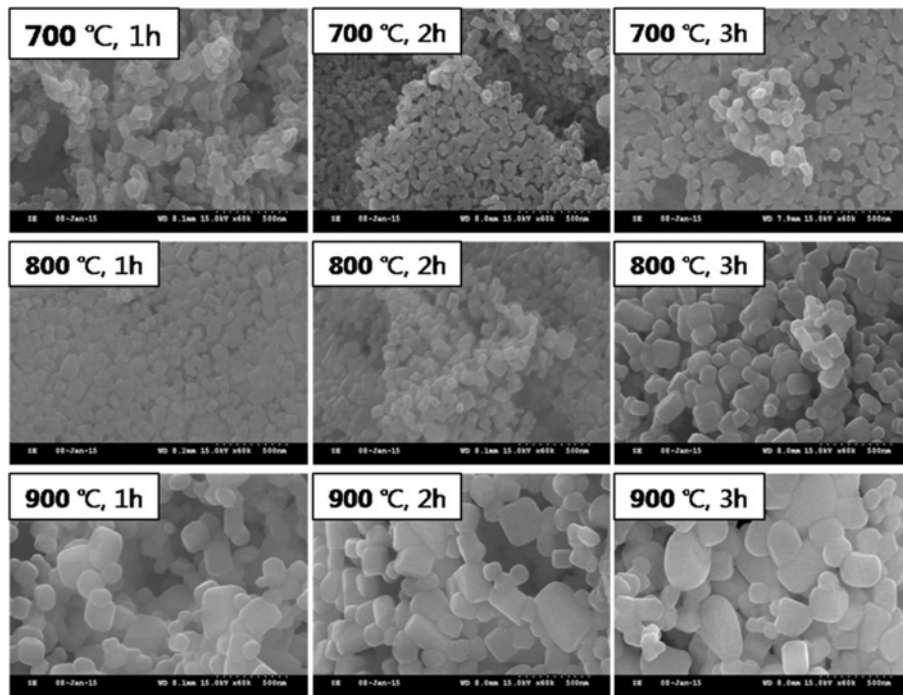


Fig. 5. FE-SEM images of MgO nanoparticles with calcination time.

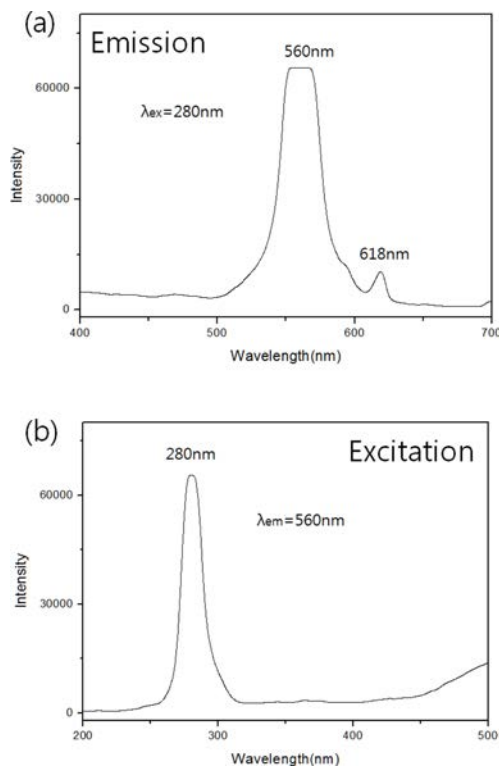


Fig. 6. The PL spectra of prepared MgO nanoparticles, (a) emission spectrum of MgO at 280 nm, (b) excitation spectrum of MgO at 560 nm.

temperature of 500 °C. However, the size of the particles (30 to 50 nm) is small, irregular and uneven, and the crystallinity is low. Most of the generated particles are granular. When the calcination temperature increased to 700 °C, the grain growth (100 to 200 nm) was observed

with increasing crystallinity and cubic crystal form was observed. In the samples fired at 800 °C, the morphology and size of the particles were remarkably changed, and the crystallization proceeded in a wider range and uniform particle size distribution started to appear. Crystallization is promoted at 800 °C or higher, and cubic type particles can be confirmed by rapid crystal growth. Fig. 5 shows SEM photographs of MgO powders calcined at 700 °C, 800 °C and 900 °C while changing the heat treatment time to 1-3 hrs. As the calcination time increased from 1 h to 3 hrs, the crystal form changed to a more perfect crystalline phase of the cubic form. Fig. 6 is a PL spectra of MgO nanoparticles synthesized by heat treatment at 500 °C, 700 °C, and 1,100 °C for 3 hrs, respectively. When the excitation wavelength was fixed at 280 nm and measured from 400 nm to 700 nm, the maximum emission wavelength was 560 nm. In addition, the maximum excitation was at 280 nm when measured from 200 nm to 500 nm with a fixed maximum emission wavelength of 560 nm.

Conclusions

MgO nanoparticles were synthesized under various conditions by impregnating starch into a $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ aqueous solution. Starch was used as a polymer matrix for impregnation, and optimum conditions for the synthesis of MgO nanoparticles were determined by controlling the heat treatment temperature and time. As a result of heat treatment at 500-1,100 °C for 1-3 hrs with different heat treatment temperature and calcination time, crystallization was accelerated and grain growth was observed with increasing heat treatment temperature

and time. As described above, it was confirmed that when the MgO nanoparticles were prepared using the liquid precursor method, the heat treatment temperature and time had an influence on the crystal growth and particle size.

Acknowledgments

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