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Synthesis, characterization and optical properties of $Mg(OH)_2$ micro-/nanostructure and its conversion to MgO

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Abstract

Magnesium hydroxide ($Mg(OH)_2$) micro- and nanostructures have been synthesized by a single step hydrothermal route. Surface morphology analysis reveals the formation of micro- and nanostructures with varying shape and size at different synthesis conditions. Structural investigations by X-ray diffraction (XRD) and transmission electron microscopy (TEM) confirm that the synthesized material is $Mg(OH)_2$ with hexagonal crystal structure. An optical band gap of 5.7 eV is determined for $Mg(OH)_2$ nanodisks from the UV–vis absorption spectrum. A broad emission band with maximum intensity at around 400 nm is observed in the photoluminescence (PL) spectra of $Mg(OH)_2$ nanodisks at room temperature depicting the violet emission, which can be attributed to the ionized oxygen vacancies in the material. Furthermore, $Mg(OH)_2$ has been converted to MgO by calcination at 450 °C. Optical studies of the MgO nanodisks have shown an optical band gap of 3.43 eV and a broadband PL emission in the UV region. $Mg(OH)_2$ and MgO nanostructures with wide-band gap and short-wavelength luminescence emission can serve as a better luminescent material for photonic applications.

Keywords: A. Powder: Chemical preparation; B. Electron Microscopy; C. Optical properties; D. MgO

1. Introduction

Recently, nanostructures of magnesium oxide (MgO) and hydroxide ($Mg(OH)_2$) have been extensively studied. Magnesium and its alloys possess unique properties such as low weight and non-toxicity. These properties are found advantageous for various devices in the fields of electronics, aerospace, automotive applications and biomedicine [1–3]. Magnesium oxide, a very important wide-band gap insulator, has been attracting much attention due to its application in catalysis [4], toxic waste remediation [5], as additives in refractory, paint, and superconductor products [6–8], and in steel manufacturing because of its high corrosion-resistant behavior [9]. Magnesium hydroxide (Brucite) is commonly used as the flame-retardant filler in composite materials due to its ability to undergo endothermic dehydration in fire conditions [10]. It has also been used as acidic waste neutralizer in environmental protection, papermaking industry, as a fertilizer additive [11–13], and as the most important precursor for the synthesis of magnesium oxide [14].

Recently, much attention has been paid to the synthesis of MgO and $Mg(OH)_2$ nanostructures. $Mg(OH)_2$ nanostructures with versatile morphological structures can be prepared by several methods, such as electrodeposition [15], sol–gel technique [16], precipitation [17], hydrothermal [18], solvothermal [19] and microwave assisted synthesis [20]. Several reports demonstrated that these structures can be converted into each other (i.e. $MgO \leftrightarrow Mg(OH)_2$) by either hydration [21] or dehydration [22] procedures. Generally, the final properties of the nanocrystals strongly depend on their shape, agglomeration state and preparation process. Hydrothermal route is one of the most extensively employed techniques in the synthesis of metal oxide nanostructures. The hydrothermal method has many advantages. For example, a highly homogeneous crystalline product can be obtained directly at a relatively lower reaction temperature; it favors a decrease in agglomeration between particles, narrow particles size distribution, phase homogeneity, uniform composition, high product purity and controlled

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particle morphology [23]. In this work, we discuss the synthesis of various nano-/microstructures of $Mg(OH)_2$ by hydrothermal technique and its conversion to MgO. Structural analysis is performed on the micro-/nanostructures of $Mg(OH)_2$. Optical properties of $Mg(OH)_2$ and MgO nanostructures are also discussed.

2. Experimental

2.1. Synthesis of magnesium hydroxide nanostructures

$Mg(OH)_2$ nanostructures were synthesized by a single step hydrothermal route. The starting materials used for the synthesis are magnesium nitrate hexahydrate ($Mg(NO_3)_2{\cdot}6H_2O$) and sodium hydroxide (NaOH). All the chemicals were analytic grade reagents (Fisher Scientific) and used without further purification. Experimental details are as follows: 0.5 M of $Mg(NO_3)_2{\cdot}6H_2O$ and 5 M of NaOH solutions were prepared in distilled water. The NaOH solution was slowly added to the $Mg(NO_3)_2{\cdot}6H_2O$ solution under manual stirring. Then, the mixture was placed in an ultrasonicator bath for about 30 min to obtain homogeneous solution. Further, 10 mL of the above solution was loaded into a 20 mL Teflon-lined autoclave, which was then filled with 2 mL of absolute ethanol as buffering agent. Finally, the autoclave was sealed and maintained at different temperatures in the range between 180 and 250 °C for 3–72 h (hydrothermal treatment time, t_H). The autoclave was then allowed to cool down to room temperature naturally. The precipitates were filtered, washed with distilled water first to remove the soluble nitrates and then with ethanol to reduce the agglomeration, and later dried at 80 °C for 1 h. The white colored material that resulted was later used for various characterizations. $Mg(OH)_2$ micro-/nanoparticles were also synthesized at 200 °C for 24 h with the addition of 0.1 g of urea and 0.1 g of PEG 2000 along with 0.4 M of $Mg(NO_3)_2{\cdot}6H_2O$ and varying molar concentrations of NaOH (0.4–2.0 M).

2.2. $Mg(OH)_2$ to MgO conversion by calcination

Some of the as-synthesized $Mg(OH)_2$ samples (at 200 °C for 3, 12 and 48 h) were subjected to calcination in a muffle furnace in air. The samples were first heated to 250 °C and held at that temperature for 1 h, then at 350 °C for 2 h, and finally at 450 °C for 2 h. The temperature was increased very slowly to avoid the sudden collapse of the Brucite structure, as well as preserve the morphological features of the micro-/nanocrystalline $Mg(OH)_2$ in the final MgO materials. In the present work, we have approached two different methods for the conversion of $Mg(OH)_2$ to MgO: (1) systematic calcination of the as-prepared $Mg(OH)_2$ material at 250–450 °C and (2) TGA measurement in the temperature range of 50–1000 °C.

2.3. Characterization

Surface morphology analysis of the $Mg(OH)_2$ and MgO materials was performed by a field emission scanning electron microscope (SEM, JEOL JSM-6330F) operated at an accelerating voltage of 15 kV. Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) images, and selected-area electron diffraction (SAED) patterns were obtained from a JEOL-2010F apparatus employing an accelerating voltage of 200 kV. Crystal structure analysis was carried out by employing an X-ray diffractometer (D-8 Bruker-AXS) equipped with a Cu Kα radiation source (λ = 1.5406 Å) and a two-dimensional area detector. A UV–vis spectrum was obtained from Perkin-Elmer Lambda 900 UV/Vis/NIR spectrometer, and the photoluminescence spectra were recorded from SPEX FluoroLog spectrofluorometer (Horiba, Jobin Yvon). For the spectroscopic analysis, nanomaterials were dispersed in NaOH solution at room temperature and taken into a quartz cell (1 cm optical path length). Thermal behavior of the $Mg(OH)_2$ micro-/nanostructures was studied through thermogravimetric analysis (TGA) data, which were collected with a TA instruments TGA 2950 apparatus under Ar flow (100 sccm), in the temperature range of 50–1000 °C. The heating rate was 25 °C/min from 50 to 250 °C with equilibrium at 250 °C, 10 °C/min from 250 to 400 °C with equilibrium at 400 °C and 25 °C/min from 400 to 1000 °C.

3. Results and discussion

3.1. Surface morphology of $Mg(OH)_2$

The surface morphology of $Mg(OH)_2$ micro-/nanostructures is analyzed from SEM images. The $Mg(OH)_2$ materials with various shapes and sizes, synthesized at different hydrothermal reaction conditions are listed in Table 1. Fig. 1 shows the SEM images of $Mg(OH)_2$ microparticles synthesized at temperatures of 180, 200, and 250 °C for 24 and 48 h, respectively. The $Mg(OH)_2$ product synthesized at 180 °C for 24 h shows wide range of size distribution from hexagonal nanodisks to microdisks, which vary from about 120 nm to 4 μm in width and 75–150 nm in thickness (Fig. 1(a)). As the synthesis time increased to 48 h (Fig. 1(b)), the surface morphology changes from micro-/nanodisks to polyhedrons, which have 14 faces. These polyhedrons also show a wide range of size distribution with varying widths of around 200 nm to 2.5 μm and thicknesses of 170 nm to ∼2 μm. At the hydrothermal treatment temperature of 200 °C, the $Mg(OH)_2$ particles still maintain polyhedron shape similar to the materials synthesized at 180 °C, but with a slight decrease in size. The polyhedrons produced at 200 °C for a hydrothermal reaction with duration of 24 h have widths of 250 nm to 2.3 μm and thicknesses of around 150 nm to 1.7 μm (Fig. 1(c)). On the other hand, the polyhedrons formed for the duration of 48 h are about 340 nm to 2.55 μm wide and 130 nm to 1.4 μm thick (Fig. 1(d)). At the highest synthesis temperature of 250 °C, the particles produced for 24 h have widths of 170 nm to 2.2 μm and thicknesses of around 125–760 nm (Fig. 1(e)). The particles at this synthesis condition have a large quantity of nanostructures rather than microstructures and also show a wide range of particle size distribution. $Mg(OH)_2$ material formed at 250 °C for 48 h are around 380 nm to 1.7 μm wide and 210 nm to