

Research Article

Synthesis of Nanocrystalline MgO Particles by Combustion Followed by Annealing Method Using Hexamine as a Fuel

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In this work, nanocrystalline MgO particles were prepared through combustion method using magnesium nitrate as oxidizer and hexamine as a fuel. The materials obtained by combustion method were subsequently annealed at 800°C for 3 h to improve the crystallinity and phase purity. The obtained MgO nanomaterials were characterized by powder X-ray diffraction analysis (XRD), infrared (IR) spectroscopy, photoluminescence (PL), near-infrared (NIR) spectroscopy, and scanning electron microscopy (SEM). The cubic crystal structure with lattice parameter, $a = 0.4210(4)$ nm with average crystalline size of 22 nm, is obtained for the nano-MgO particles. The PL emission spectrum of nanocrystalline MgO materials exhibits three emission peaks at 432, 465, and 495 nm which are due to various structural defects. The SEM results expose the fact that the MgO nanomaterials are seemingly porous and highly agglomerated with fine particles. Owing to the higher reflectance of prepared nanocrystalline MgO, it can be used as NIR reflective pigments. The present results prove that the combustion technique using hexamine can produce the materials with high crystallinity. To the best of our knowledge, this is the first report on the synthesis of nanocrystalline MgO materials by combustion method using hexamine as a fuel.

1. Introduction

Magnesium Oxide (designated as MgO) is a semiconductor/insulator which crystallizes in rock salt/sodium chloride (NaCl) type cubic structure [1]. Like MgO, many binary oxides, for instance, CaO, SrO, BaO, NiO, and CoO, also crystallize in rock salt structure [1]. MgO is an attractive material which has many potential applications [2–15], such as water purification, optoelectronics, microelectronics, and additive in heavy fuel oil, paint, gas separation, bactericides, and insulator in industrial cables, crucibles, and refractory materials. Further, it has been used as an oxide barrier in spin tunneling devices as well as substrate in super conducting and ferroelectric film. The MgO nanoparticles have high catalytic activity. Due to high specific surface area of nano-MgO materials, they are found to catalyze efficiently in variety of organic reactions [16–18].

Several preparation routes [2–6, 9, 19–31], namely, combustion, microwave assisted synthesis, spinning disk reactor,

wet chemical method, nonaqueous sol-gel method, chemical synthesis, microwave assisted sol-gel synthesis, surfactant assisted precipitation method, electrospinning technique, colloidal synthesis, *rf* impulse discharge plasma, hard templating pathway, sol-gel method, and microwave hydrothermal process, have been reported for the preparation of nano-MgO materials. For these synthesis methods, in literature, there are a variety of precursors, namely, magnesium nitrate, glycine, Mg(CHCOO)₂ and ethylene glycol, MgCl₂ and NaOH, magnesium foil, toluene and MgCl₂·6H₂O, ammonia, polyvinyl alcohol, polyvinyl pyrrolidone, magnesium acetate tetrahydrate, Mg particle, tungsten wire, trioctylphosphine oxide (TOPO) and bis(cyclopentadienyl)magnesium (Cp₂Mg), Mg rod electrode, and magnesium acetate, which have been reported for the preparation of MgO nanoparticles. Further, to prepare MgO nanomaterials, various fuels [2–15], namely, glycine, urea, combination of urea, glycine, and cellulose, propane, and 1,3 propane diol, have been used. Among these different fuels, urea [4, 8, 10–12, 14, 15] is

the most commonly used fuel in the preparation of nano-MgO particles. In literature, for the synthesis of nano-MgO materials, magnesium nitrate and urea with the molar ratio 1:1.67 have been used as the oxidizer and fuel, respectively [4, 8, 10–12, 14, 15]. The (average) crystalline sizes of 15–60 nm [7], 16–19 nm [11], and 38 nm [14] have been reported for the MgO particles by different research group. The particle size obtained from microimages (SEM/TEM) has showed 300–350 nm (SEM) [7] and 20–25 (TEM) [4]. The combination of urea, glycine, and cellulose with the molar ratios 1:1.67:1.11:0.42 has showed the lowest particle size of 6.9 nm (XRD) and 5 nm (TEM) [6]. In addition to the reported various fuels [2–15], there are several efficient fuels which are available to perform the combustion synthesis. Hexamine is one of the efficient fuels to synthesize the nanoscale materials. To the best of our knowledge, there is no report available in literature on the synthesis of nano-MgO materials by hexamine as the fuel by combustion method. In this paper, we report the synthesis and characterization of nanocrystalline MgO particles by combustion method using hexamine as a fuel and magnesium nitrate as the precursor.

2. Experimental Procedure

The nanocrystalline MgO particles were prepared by combustion method using magnesium nitrate and hexamine (see the flow chart in Figure 1). The commercially available $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was first dissolved in minimum quantity of deionised water. Then this solution was stirred at 300 rpm for few minutes. After that, the fuel, hexamine ($\text{C}_6\text{H}_{12}\text{N}_4$), dissolved in minimum quantity of deionised water was mixed to the magnesium nitrate solution and stirred well. Then, the solution combustion mixture was heated slowly in heating mantle until it gets ignited. When the temperature reached about 190°C , combustion flame appeared. Figure 2 shows the observation of flame during the combustion of nitrate and fuel. After completion of combustion, the crude brown color powder was obtained. The obtained combustion product was annealed at 800°C for 3 hrs in a groove rolled muffle furnace. After completion of annealing, the furnace was cooled to room temperature by switching off the power. The annealed product was white in color and taken for characterizations. The phase identification and purity of the annealed materials were tested by powder XRD and FT-IR spectroscopy. The photoluminescence (PL) property of the MgO powder sample was performed in a spectrofluorometer (ELICO SL 174) using 150 Watt Xenon Arc lamp as the excitation light source. The NIR spectrum of MgO powder was performed in a NIR Spectrophotometer (ELICO SL 153) using Quartz halogen lamp as the light source. The microstructural images and the elements present in the combustion-annealed MgO materials were performed in the scanning electron microscope, SEM (Jeol model; JSM-6390LV), attached with Energy Dispersive X-ray Analyzer (JED-2300).

3. Results and Discussion

3.1. XRD Pattern of Nano-MgO Powder. In the present work, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is used as oxidizer and $\text{C}_6\text{H}_{12}\text{N}_4$ is used as

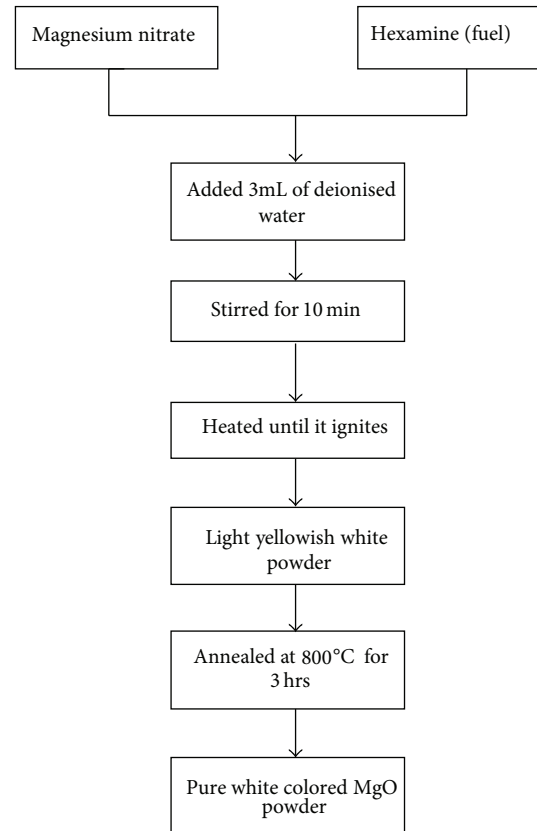


FIGURE 1: Experimental flow chart for the synthesis of MgO nanopowders by combustion followed by annealing method.

reducing agent. Similar to the oxidation number concept, the valency of the oxidizing elements is considered as negative and the reducing elements as positive in solution combustion calculations [32]. Accordingly, the elemental valency of C, H, and Mg is +4, +1, and +2, respectively, and the oxidizing valency of oxygen is taken as -2 . The valency of nitrogen is assumed to be zero. Based on this concept, the oxidizing valency of magnesium nitrate and the reducing valency of hexamine can be calculated as $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} = [+2 - 12 + 0] = -10$ and $\text{C}_6\text{H}_{12}\text{N}_4 = +24 + 12 + 0 = 36$. According to the equivalence ratio theory, for the combustion of magnesium nitrate and hexamine mixture, the molar ratio becomes $10/36 = 0.28$.

That is, $\Phi_e = \frac{\sum(\text{Coefficient of oxidizing elements in specific formula} * \text{valency})}{(-1) \sum(\text{Coefficient of reducing elements in specific formula} * \text{valency})} = 10/36 = 0.28$. The 1:0.28 molar ratio of nitrate and hexamine is taken for the formation of MgO in the present combustion reaction. In order to see the variation in fuel concentration on the phase purity and particle size of MgO nanomaterial under different molar ratios, for example, 1:0.1, 1:0.2, 1:0.28, 1:0.4, 1:0.5, 1:0.75, and 1:1 conditions, the combustion syntheses were carried out. However, no significant effects are seen on their physical properties.

The powder XRD analyses were performed in the 2θ range between 20 and 80° using Cu K_α radiation. In Figure 3,

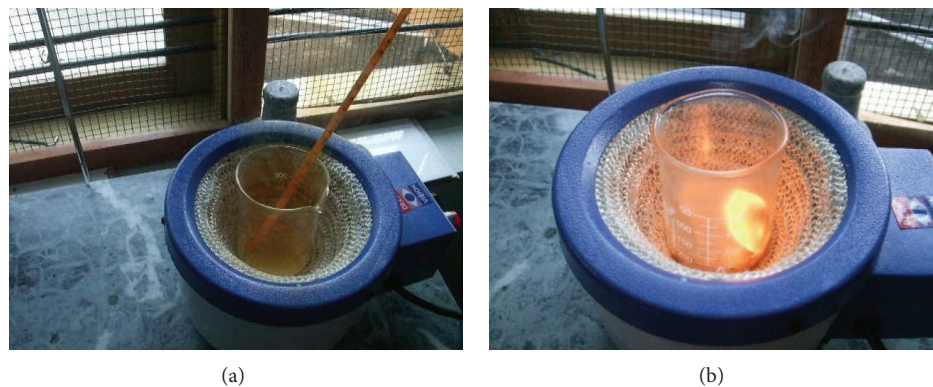


FIGURE 2: Slow evaporation (a) and observation of flame during combustion between nitrate and fuel (b) in the synthesis of MgO.

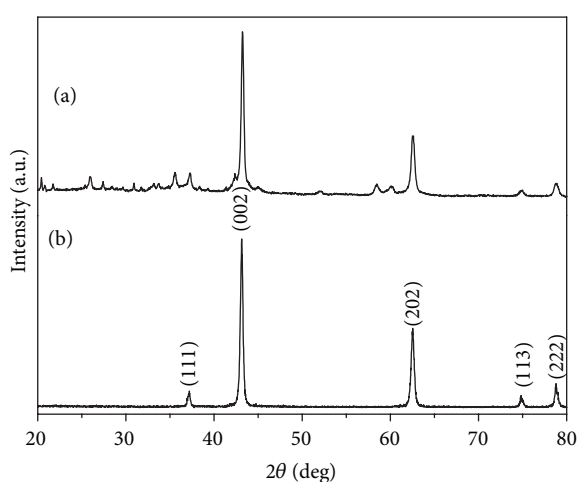


FIGURE 3: XRD patterns of as-prepared (a) and annealed (b) MgO nanoparticles.

the powder XRD patterns of both as-prepared and annealed MgO nanopowder are presented. From these XRD patterns, we observe that the annealed material is crystallized in single phase with cubic symmetry. The Bragg reflections are indexed on the basis of space group, Fm-3m (225), $Z = 4$ with cubic lattice parameter, and $a \sim 0.4210(4)$ nm for the annealed sample. This present value is in good accordance with the literature reports. The Bragg reflections such as (111), (002), (202), (113), and (222) are seen in the 2θ range between 20 and 80° . All reflections are sharp with slight broadening. These reflect the crystalline nature of MgO nanopowder. The average crystalline size of 22 nm is obtained for the annealed nanocrystalline MgO powder from the Debye Scherrer formula using the XRD powder data [33].

3.2. FT-IR Spectrum of Nano-MgO Powder. The typical FT-IR spectrum for the annealed MgO powder is depicted in Figure 4. From FT-IR analysis, the stretching vibration mode for the Mg-O-Mg compound is seen in the range of $487\text{--}677\text{ cm}^{-1}$ as a broad band. Two distinct bands are seen at the wave number ranges of $1014\text{--}1073\text{ cm}^{-1}$ and $1567\text{--}1641\text{ cm}^{-1}$ and are attributed to the bending vibration of absorbed water

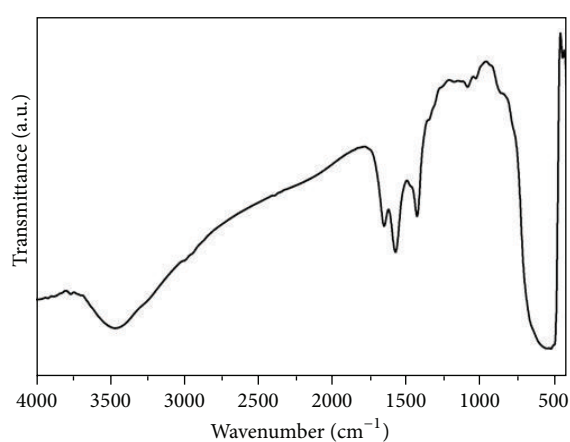


FIGURE 4: FT-IR spectrum of annealed MgO nanoparticles prepared by combustion followed by annealing method.

molecule and surface hydroxyl group ($-\text{OH}$), respectively. A broad vibration band is seen in the wavenumber range $3325\text{--}3650\text{ cm}^{-1}$ due to O-H stretching vibration of absorbed water molecule and surface hydroxyl group [11]. This is due to the aerial adsorptions of water molecule onto the MgO surface when it is exposed to atmosphere. The FT-IR absorption peak seen at the wavenumber 1420 cm^{-1} is assigned to the asymmetric stretching of the carbonate ion, CO_3^{2-} species [11].

3.3. Optical Properties of Nano-MgO Powder. The PL emission spectrum of annealed nanocrystalline MgO powder is shown in Figure 5. The PL emission spectrum was recorded at 385 nm as an excitation wavelength with bandwidth equal to 5 nm and scanning rate equal to 200 nm/sec. The PL emission spectrum reveals three emission peaks at 432, 465, and 495 nm in 400–500 nm emission band range, in which the 432 nm emission arises from the defect band transition and $^3\text{B}_{1u} \rightarrow ^1\text{A}_g$ from F_2^{2+} defect centre occupied in D_{2h} symmetry [11, 34]. The 465 and 495 nm blue emissions are owing to the recombination of electrons with oxygen vacancies (i.e., F centre). These vacancies are possibly generated

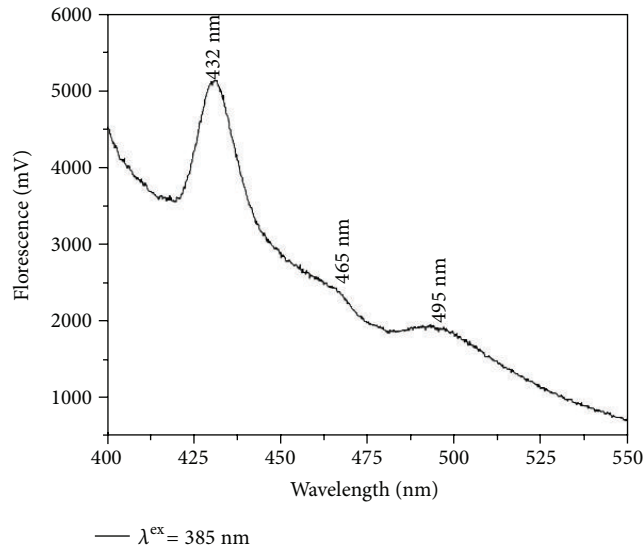


FIGURE 5: Room temperature PL spectrum of annealed MgO nanoparticles under the excitation wavelength of 385 nm.

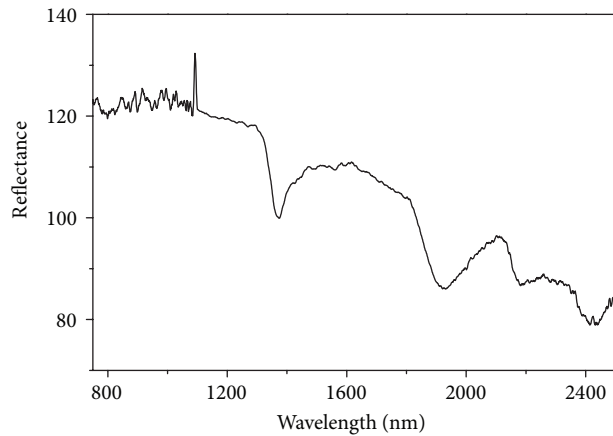


FIGURE 6: NIR spectrum of annealed MgO nanoparticles prepared by combustion followed by annealing method.

by various factors, namely, unbalanced oxygenation during self-ignition, subsequent crystallization process, and Mg vacancies and interstitials [11, 35]. Figure 6 depicts the NIR spectrum of annealed nano-MgO powder as a function of wavelength. Quite similar to the report of Jeevanandam et al. [36], our NIR spectrum of nano-MgO powder shows higher reflectance value in the region 800–1300 nm. This is due to the smaller crystalline size of combustion-annealed nano-MgO powder. Owing to the higher reflectance of nano-MgO, it can be used as NIR reflective pigments [36].

3.4. Microstructure Analysis of MgO by SEM. In order to see the morphology and the particle size of the annealed MgO, the SEM images were taken in the scanning electron microscope (SEM; Jeol model JSM-6390LV instrument) (see Figures 7(a)–7(d)). The SEM images are shown in different magnifications. The SEM results reveal that the annealed MgO nanomaterials are seemingly porous and highly agglomerated with the nanoentities. Thus the particle

size of MgO could not be seen accurately from the present SEM results (Figure 8). Due to the porous nature of MgO, the combustion-annealed MgO nanomaterials may play a major role in gas sensing application.

4. Conclusion

From our present work, it is concluded that it is easy to prepare MgO nanoparticles by combustion method using magnesium nitrate as oxidizer and hexamine as a fuel. The obtained white color MgO materials were analyzed using various characterization techniques. The XRD pattern confirmed the crystallinity and phase purity of the annealed nano-MgO powder. The average particle size calculated from the diffraction peaks was found to be 22 nm. The SEM result revealed that the powder is porous and agglomerated with polycrystallite nanoparticles. The MgO materials obtained by combustion-annealing method using hexamine may prove

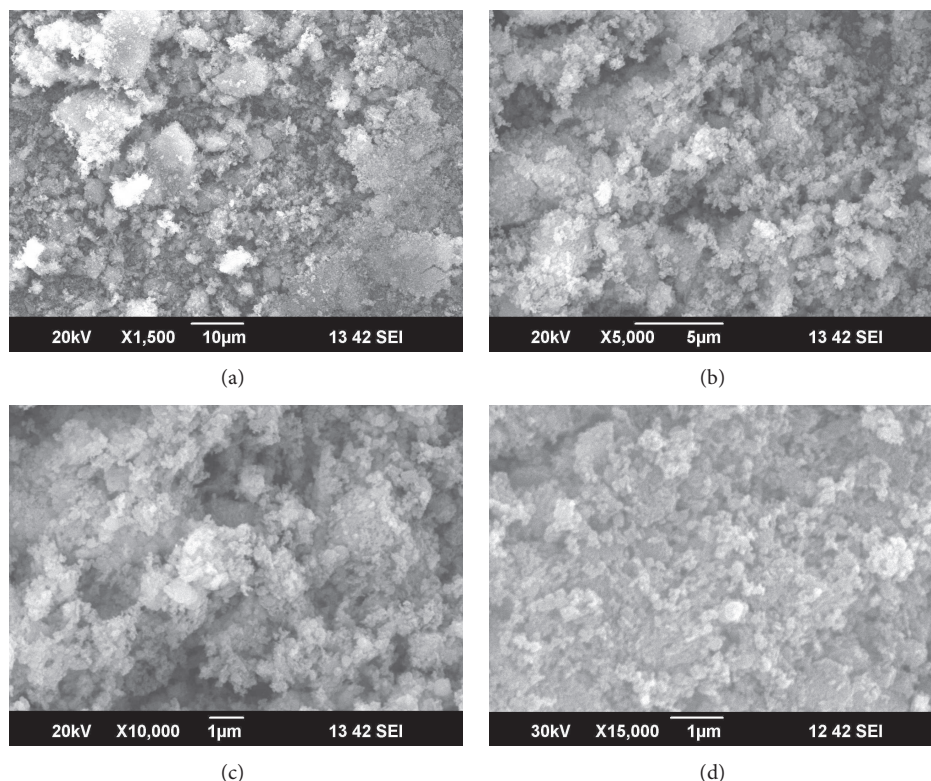


FIGURE 7: (a–d) SEM microimages of annealed MgO nanopowders obtained by combustion followed by annealing method.

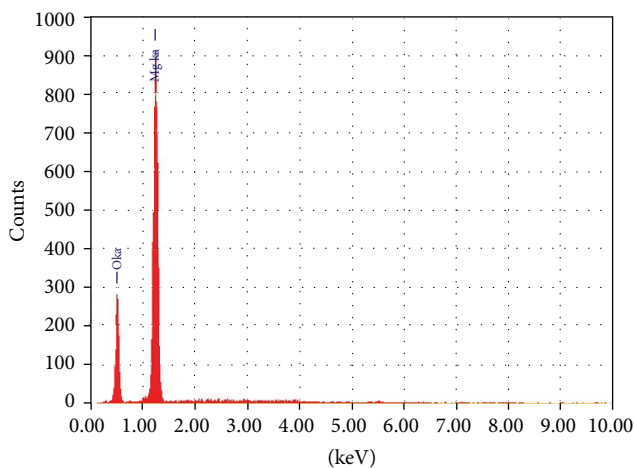


FIGURE 8: EDX spectrum of annealed MgO nanopowders.

potential applications in pigments, catalyst, water purification, optoelectronics, bactericides, substrate, insulator, crucibles, and refractory materials.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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