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Synthesis of magnesium oxide particles with stacks of plates morphology

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ABSTRACT

Magnesium oxide particles with a new morphology of stacks of plates have been prepared through a precursor method. Magnesium oxalate dihydrate, prepared by the reaction of an aqueous concentrated solution of magnesium chloride with macro-crystalline magnesium oxide followed by ammonium oxalate treatment, was used as the precursor. The magnesium oxide particles with the morphology of stacks of plates were obtained by calcination of the magnesium oxalate dihydrate at 500 °C for 3 h. The products were characterized by an array of analytical techniques. The morphology of prepared MgO is different from other known morphologies of magnesium oxide.

1. Introduction

Magnesium oxide possesses interesting properties and potential applications in the areas such as pharmaceuticals [1], electro-optical devices [2], fluorescent displays [3], ferroelectric materials [4], etc. Magnesium oxide is also used in superconducting films as a substrate [5], and lithium ion batteries [6]. Moreover, ultrafine magnesium oxide is currently used as bactericide [7], adsorbent [8] and catalyst [9,10].

The synthesis of magnesium oxide particles with unique morphologies has recently attracted much attention since the physicochemical properties of MgO can depend on morphologies [11,12]. Various synthetic methods such as chemical vapor deposition, template synthesis, precursor decomposition, ion-sputtering, homogeneous precipitation, sol–gel processing, precipitation pyrolysis, epitaxial growth and melt synthesis have been developed for the controlled synthesis of MgO particles [13–20]. The commonly observed morphologies of magnesium oxide include cubes [17], whiskers/fibers [20], nanosheets/nanoplates/nanoflakes [21], flower-like [22], nanorods [23], nanotubes/microtubes [24,25], spheres [26], nanobelt [27], lamella-like [28], corraline [29], rectangular parallelepiped [30], rectangular sheets [31], tubular tetrapod [32], and columnar structure [33]. In the present study, magnesium oxide with a unique morphology of stacks of plates has been synthesized using a precursor approach and to the best of authors' knowledge, this is the first time such a morphology is reported.

2. Experimental

All the reagents were analytical grade and were used as received. The precursor, magnesium oxalate dihydrate, was prepared first and it was calcined at 500 °C for 3 h inside a muffle furnace to yield magnesium oxide. More details are as follows.

About 37.5 g magnesium chloride hexahydrate was dissolved in about 62.5 ml of de-ionized water in a conical flask and heated to 70 °C. After reaching 70 °C, macro-crystalline magnesium oxide (0.225 g) was added in about 30 min in 5 min intervals and the contents were stirred for about 21 h. A gel was obtained which was cooled to room temperature. The gel is known to be made up of magnesium oxychloride [23]. For the preparation of magnesium oxalate dihydrate, about 5 ml of the gel was added into about 100 ml of 0.1 M ammonium oxalate aqueous solution and the contents were kept for 24 h for equilibrium at room temperature. The contents were centrifuged, washed with water four times followed by ethanol, and dried in an oven. The magnesium oxalate dihydrate thus obtained will be henceforth referred to as magnesium oxalate-1 and it was used as the precursor to magnesium oxide-1. For comparison, a magnesium oxalate dihydrate sample (henceforth be referred as magnesium oxalate-2) was prepared via direct precipitation by adding about 100 ml of 0.1 M magnesium chloride aqueous solution into 100 ml of 0.1 M ammonium oxalate aqueous solution in a drop wise manner at room temperature. After the addition of ammonium oxalate is complete, the contents were stirred for 6 h at room temperature. A precipitate was obtained which was centrifuged, washed with water and alcohol and finally dried in the oven. Magnesium oxalate-2 was also calcined at 500 °C for 3 h to yield magnesium oxide-2. In addition, magnesium oxalate dihydrate, obtained commercially, was also calcined at 500 °C to obtain magnesium oxide-3 for comparison with the other two magnesium oxide samples, i.e. MgO-1 and MgO-2. Emphasis was made with reference to detailed characterization on magnesium oxalate-1 and MgO-1 due to their unique morphologies.

Powder X-ray diffraction (XRD) measurements were carried out on a Bruker AXS D8-Advance powder X-ray diffractometer with Cu-Kα radiation ($\lambda = 1.5418$ Å) with a scan speed, 2°/min. TGA measurements were carried out on a Perkin Elmer Thermal Analyzer (Pyris Diamond) under air with a heating rate of 10°/min in the temperature range, 25–500 °C. The morphologies of magnesium oxalate dihydrates and the magnesium oxides were observed using a field emission scanning electron microscope (FEI Quanta 200F) operating at an accelerating voltage of 20 kV. FT-IR measurements were done using a Thermo Nicolet Nexus FT-IR spectrometer using KBr technique.

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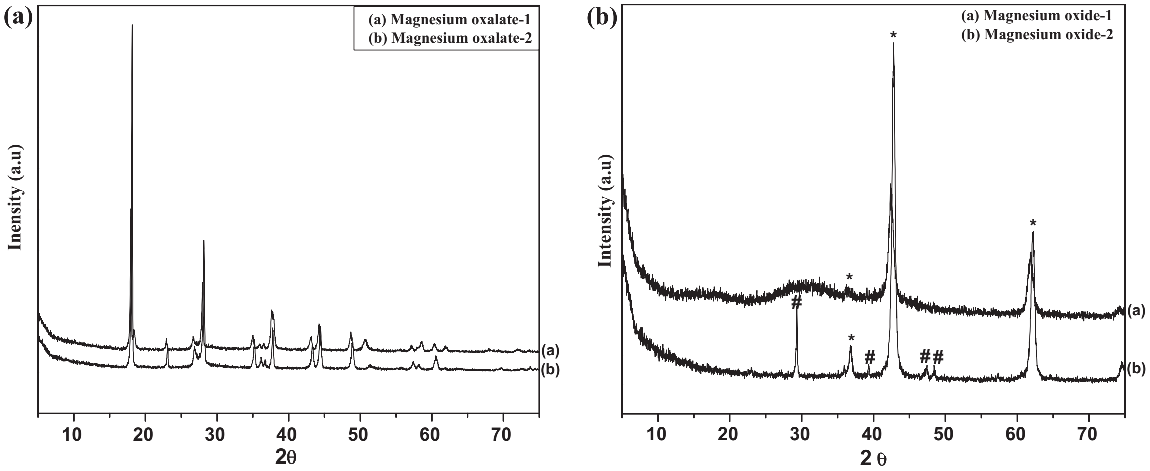


Fig. 1. Powder X-ray diffraction patterns of (a) magnesium oxalate-1 and magnesium oxalate-2 and (b) magnesium oxide-1 and magnesium oxide-2. The peaks due to MgO are indicated by '*' and those due to magnesium oxalate are indicated by '#'.

3. Results and discussion

The powder XRD patterns of magnesium oxalate-1 and magnesium oxalate-2 and the corresponding magnesium oxides (MgO-1 and MgO-2), which were obtained from the calcination of the precursors, are shown in Fig. 1. The peaks in the XRD patterns confirmed the formation of magnesium oxalate dihydrate (JCPDS file: 23-0395) and magnesium oxide (JCPDS file: 78-0430). The XRD pattern of magnesium oxide-2 shows some additional minor peaks due to magnesium oxalate which indicate the incomplete conversion of magnesium oxalate-2 to MgO-2 under similar calcination conditions. Fig. 2 shows the TGA patterns of magnesium oxalate-1 and magnesium oxalate-2. They show two weight loss steps; one at about 225 °C and another at 498 °C. The first step with a weight loss of about 23.6% is attributed to the removal of two water molecules from magnesium oxalate dihydrate and the second step with a weight loss of about 47.5% is attributed to the conversion of anhydrous magnesium oxalate to magnesium oxide. The observed weight losses are in agreement with the calculated weight losses of 24.3% and 48.5% corresponding to the removal of water molecules and the conversion of anhydrous magnesium oxalate to magnesium oxide, respectively. Fig. 3 shows the FT-IR spectrum of magnesium oxalate-1 and magnesium oxalate-2 and the corresponding magnesium oxides (MgO-1 and MgO-2).

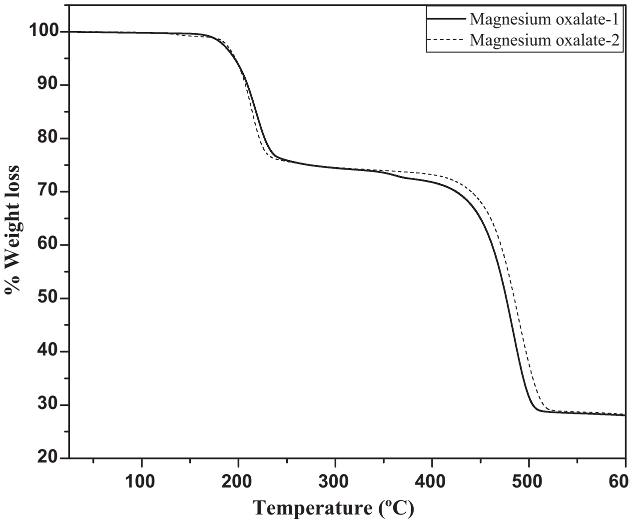


Fig. 2. The TGA curves of magnesium oxalate-1, and magnesium oxalate-2.

The assignments were made according to the literature [34–36]. The FT-IR spectra of magnesium oxalates show strong bands at about 3438 cm^{-1} which are attributed to hydroxyl stretching. The spectra show asymmetrical stretching vibration band of the carbonyl group of oxalate groups at 1653 cm^{-1}. The doublet peaks observed at about 1487 cm^{-1} and 1425 cm^{-1} are attributed to the symmetrical $\nu_s(\text{C—O}) + \nu(\text{C—C})$ vibrations. The IR bands at about 1379 cm^{-1} and 1329 cm^{-1} in magnesium oxalate-2 are attributed to $\nu_s(\text{C—O}) + \delta(\text{OC=O})$ mode. The bands at about 829 cm^{-1} and 504 cm^{-1} are attributed to the Mg—O vibration and the liberation

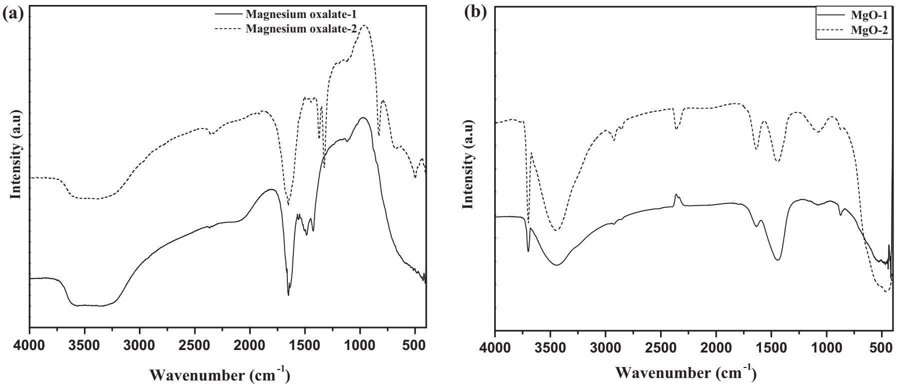


Fig. 3. FT-IR spectra of (a) magnesium oxalate-1 and magnesium oxalate-2 and (b) magnesium oxide-1 and magnesium oxide-2.

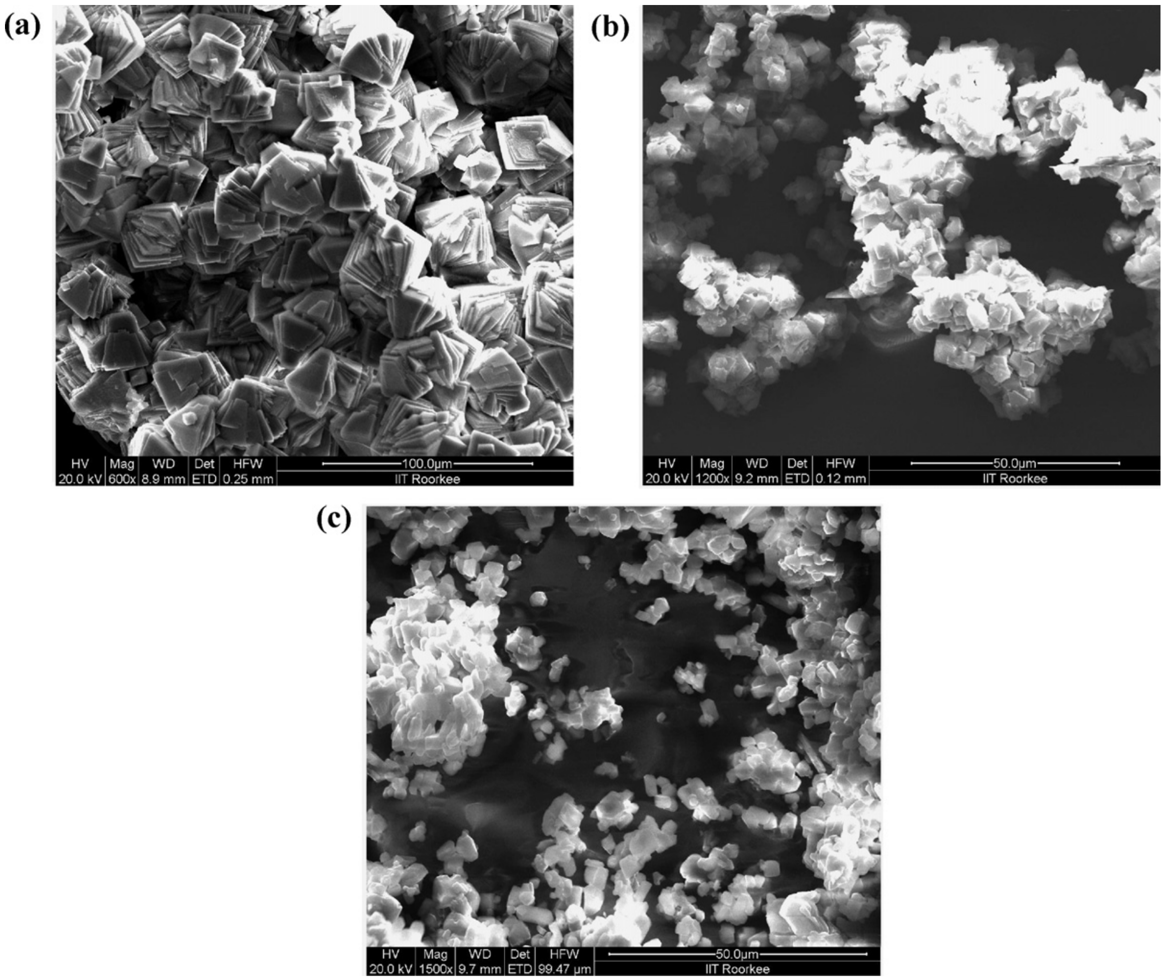


Fig. 4. FE-SEM images of different magnesium oxalate dihydrates: (a) magnesium oxalate-1 (b) magnesium oxalate-2, directly prepared from magnesium chloride and ammonium oxalate and (c) commercial magnesium oxalate dihydrate (magnesium oxalate-3).

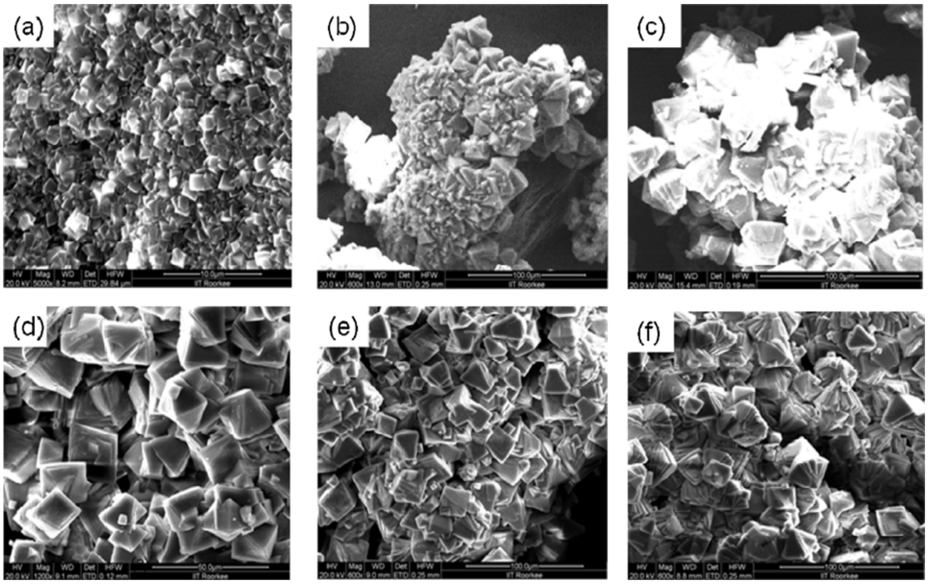


Fig. 5. FE-SEM images at different time periods during the formation of magnesium oxalate-1: (a) 1 h (b) 2 h (c) 3 h (d) 6 h (e) 18 h and (f) 24 h.

mode of water, respectively. The magnesium oxides which were obtained on calcination of magnesium oxalates show IR bands at about 3700 cm^{-1}, 3441 cm^{-1}, 1638 cm^{-1}, 1441 cm^{-1}, 1075 cm^{-1} and 870 cm^{-1}. These bands are attributed to hydroxyl stretching, hydroxyl bending, symmetric stretching of surface carbonate groups, and Mg—O vibrational modes.

Fig. 4 shows the FE-SEM images of magnesium oxalate-1 along with other types of magnesium oxalate dihydrates, i.e. the magnesium oxalate dihydrate prepared under direct precipitation (magnesium oxalate-2), and the commercial magnesium oxalate dihydrate (magnesium oxalate-3). Magnesium oxalate-1 shows an interesting morphology of stacks of plates. The plates show interaction among them forming stacks of plates. The thickness of the plates is about 2 μm and the length of the plates is about 20 μm. On the other hand, the FE-SEM image of magnesium oxalate-2 shows aggregated small cubic structures. The FE-SEM image of commercial magnesium oxalate dihydrate shows particles with an irregular morphology. To understand the time period required for the formation of magnesium oxalate dihydrate with stacks of plates morphology (magnesium oxalate-1), the reaction of magnesium oxychloride gel with ammonium oxalate at different reaction time periods (1–24 h) was carried out and FE-SEM analysis was done at various stages. Fig. 5 shows the FE-SEM images at different stages of the reaction. When the reaction was carried out for 6–24 h, product with well defined morphology of stacks of plates was obtained. However when the reaction was carried out for 1–3 h, the particles do not possess the stacks of plates morphology.

Fig. 6 shows the FE-SEM images of magnesium oxide particles obtained after calcination of the three different magnesium oxalate dihydrates (magnesium oxalates, 1–3) at 500 °C for 3 h. In the case of MgO-1, obtained from magnesium oxalate-1, the particles maintain the same morphology (i.e. stacks of plates) after heat treatment of the precursor (magnesium oxalate-1). On the other hand, MgO-2, obtained from the calcination of magnesium oxalate-2, possesses the morphology of aggregated small plates. The MgO-3 particles, obtained by the calcination of commercial magnesium oxalate dihydrate consist of irregular shaped aggregates. Fig. 7 shows the EDXA data for magnesium oxide-1 as well as the magnesium oxalate-1 and the EDXA data confirms the formation of MgO from magnesium oxalate dihydrate-1.

Various authors have reported the formation of magnesium oxide with different morphologies from magnesium oxalate dihydrate. For example, magnesium oxide has been calcined to yield nanocrystalline MgO with the morphology of small distorted rods [34]. Audebrand et al. [37] has reported the formation of MgO nanocrystallites with spherical shape via the calcination of magnesium oxalate dihydrate. Putanov et al. [38] has reported the

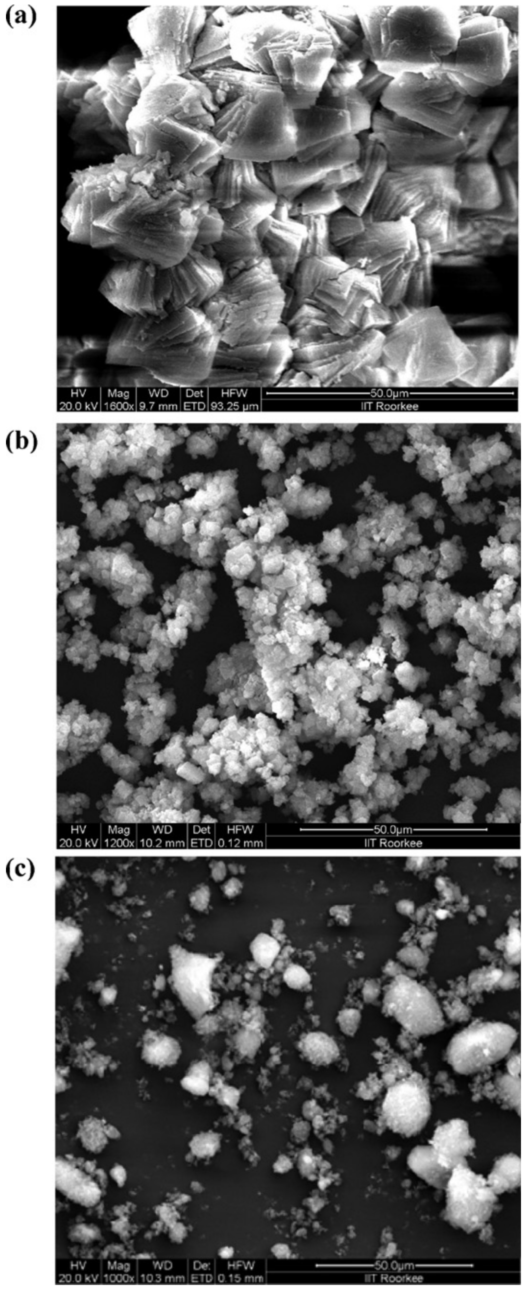
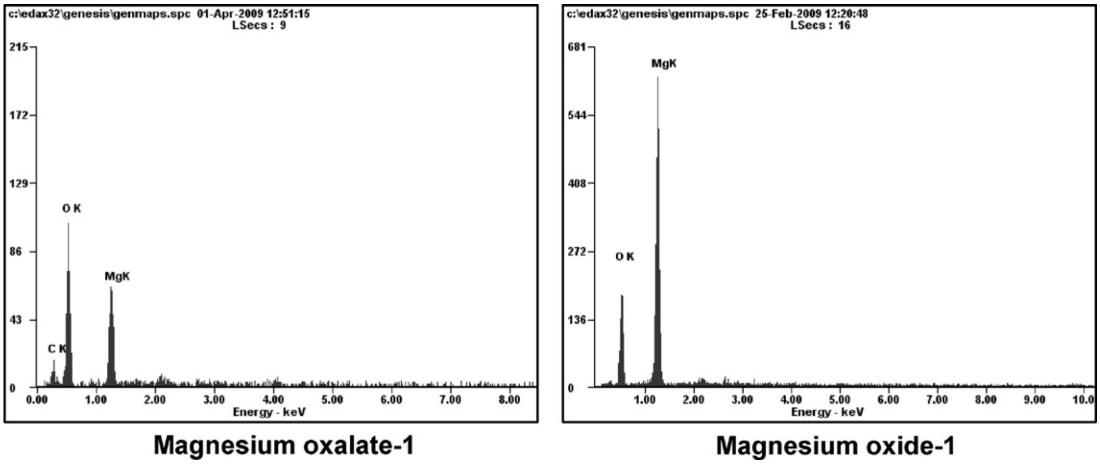


Fig. 6. FE-SEM images of magnesium oxides obtained after calcination of magnesium oxalate dihydrates at 500 °C for 3 h (a) MgO-1, (b) MgO-2 and (c) MgO-3.



Magnesium oxalate-1

Magnesium oxide-1

Fig. 7. EDXA data for magnesium oxalate-1 and the corresponding magnesium oxide-1.

formation of MgO particles with parallelepiped morphology. Guan et al. has reported the formation of MgO particles with wormhole-like porous structures [39]. The morphology of stacks of plates, observed in the present study, is quite new. It is not clear, at the present stage, why such morphology of stacks of plates is observed for magnesium oxalate-1, prepared by the reaction of magnesium oxychloride gel with ammonium oxalate and its subsequent conversion to magnesium oxide-1. It was not possible to get the FE-SEM images for the magnesium oxychloride gel since it was found to decompose on drying to yield hygroscopic magnesium chloride. However, it is known from literature [23] that magnesium oxychloride possesses rod-like morphology and it is proposed that such morphology exists for the magnesium oxychloride gel prepared in the present study. The gel which consists of rods, on reaction with ammonium oxalate, produces magnesium oxalate dihydrate with stacks of plates morphology. On calcination, this morphology is retained in the magnesium oxide.

4. Conclusions

Magnesium oxide particles with a unique morphology of stacks of plates were successfully synthesized by the calcination of magnesium oxalate dihydrate which was prepared by the reaction of magnesium oxychloride gel with ammonium oxalate. The synthetic method is simple, economical and led to MgO particles with controlled morphology. This unique morphology may be used as a substrate for the deposition of optically or magnetically interesting metal/metal oxide nanoparticles which will be carried out in the future.

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