Fabrication of light-emitting porous hydromagnesite with rosette-like architecture

Qing Li\textsuperscript{a}, Yi Ding\textsuperscript{a}, Guihua Yu\textsuperscript{a}, Cun Li\textsuperscript{a}, Fanqing Li\textsuperscript{b}, Yitai Qian\textsuperscript{a,b,\ast}

\textsuperscript{a}Department of Chemistry, University of Science and Technology of China, Hefei 230026, People’s Republic of China
\textsuperscript{b}Structure Research Laboratory, University of Science and Technology of China, Hefei 230026, People’s Republic of China

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Abstract

Porous hydromagnesite with rosette-like morphologies has been synthesized at 100 °C by a convenient hydrothermal method with the absence of additives or organic surfactants. The hydromagnesite particles are spherical with a diameter of about 250 \mu m. The thermal behavior of the product has been investigated by TGA-DTA technique, whilst the decomposition mechanism was confirmed by in situ high temperature X-ray diffraction analysis. The as-prepared hydromagnesite was found to have a photoluminescent emission at about 448 nm.

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1. Introduction

Materials with porous periodic structure are currently of great interest because of their wide range of application in separation, catalysis, optical information and host-guest chemistry [1–4]. For the design of such materials with optimal performance, the ability to control the organization and patterning of inorganic frameworks on all length scales is crucial [5]. Considerable synthetic effort has been devoted to developing porous frameworks at the multiple length scale [6–15]. Normally, organic templates were employed in the synthesis of porous materials. However, organized chamber-like architectures were prone to be destroyed after the organic content was removed. Thus the fabrication of hierarchically ordered structures has remained an experimental challenge.

Hydromagnesite (Mg\textsubscript{5}(CO\textsubscript{3})\textsubscript{4}(OH)\textsubscript{2}4H\textsubscript{2}O), the only species stable under atmospheric conditions in the big family of basic magnesium carbonates, has now been accepted as an important mineral in geology and planetology [16,17]. It has also been widely applied in industry as a fire retardant [18], as a filler for rubber and plastic [19], and as a magnesium source to prepare other magnesium compounds [20]. This material has been attracting attention of scientists from various fields. For example, V.R. Choudhary studied the thermal behavior of basic magnesium carbonate [21]; Garrel et al. measured its solubility in 1960 [22]; Donald Langmuir studied the stability of carbonate in MgO–CO\textsubscript{2}–H\textsubscript{2}O system and gave the value of free energy of formation of hydromagnesite [23]. Besides, the crystal structure of hydromagnesite was given by M. Akao [24]; the IR characterization was performed by W.B. White [25]; and the transformation of nesquehonite into hydromagnesite was investigated by P.J. Davies [26]. However, hierarchically ordered porous hydromagnesite, which exhibits interesting luminescent properties, to our knowledge, has not yet been studied. Herein, we report a simple hydrothermal route to synthesize porous hydromagnesite with a rosette-like structure. In this method, no additives or organic templates were needed. The product was found to have photoluminescent emission, which may have potential application on the design of safe, inexpensive and environmental benign optical materials.
2. Experimental

Preparation of porous hydromagnesite. Hydromagnesite samples were synthesized by a hydrothermal method. All reagents were analytical grade pure and were purchased from Shanghai Chemical Co. Ltd. In a typical procedure, 0.6 g anhydrous magnesium sulfate and 1.2 g urea were added into a Teflon-lined autoclave of 60 ml capacity. Then, the autoclave was filled with distilled water up to 85% of the total volume. The autoclave was then sealed into a stainless steel tank and maintained at 100 °C for 5–24 h without shaking or stirring. After the autoclave was cooled to room temperature naturally, a loose, white precipitate was filtered and washed with distilled water and absolute ethanol, and then dried in a vacuum at 60 °C for 5 h.

Characterization. X-ray powder diffraction (XRD) was obtained with an MXP18AHF X-ray diffractometer (MAC Science Co. Ltd) with Cu Kα radiation (λ = 1.54056 Å). The samples were scanned at a scanning speed of 0.02° s⁻¹ in the 2θ range of 10–70°. Measurement of in situ high temperature X-ray diffraction (HTXRD) were carried out in the temperature range of 100–600 °C in air, using the same instrument and performing at 18 kV (40 kV–100 mA) with a scanning speed of 8° min⁻¹.

Scanning electron microscopy (SEM) micrographs were taken using a Hitachi X-650 scanning electron microanalyzer.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) traces were collected with a Shimadzu-50 thermoanalyzer under N₂ flow at 10 °C min⁻¹ in the temperature range of 20–1000 °C.

Photoluminescent (PL) emission spectra were performed on solid samples at room temperature with a Hitachi 850 fluorescence spectrophotometer.

3. Results and discussion

3.1. XRD and SEM analysis

Fig. 1 is the XRD pattern of the sample prepared at 100 °C for 10 h under hydrothermal conditions. All diffraction peaks can be indexed as the monoclinic Mg₅(CO₃)₄(OH)₂·4H₂O and the cell parameters calculated from these diffraction data are a = 10.09 Å, b = 8.93 Å, c = 8.35 Å, and β = 113.79°, which is in good agreement with the reported data (JCPDS file number 25-513). The shape of the peak indicates the hydromagnesite sample is well crystallized.

The SEM graph of this sample is shown in Fig. 2. It exhibits an interesting spherical morphology, which consists of a rosette-like microstructure of irregular-shaped columnar pores with crystalline walls interconnected to each other. The sample was uniform with the average size of about 250 μm.
3.2. TGA and DTA analysis

The thermal behaviors of the product were explored by TGA and DTA techniques. The TG curve for the pyrolysis of as-prepared hydromagnesite is shown in Fig. 3. One can see from this figure that three mass-loss steps take place. In the temperature range from 53 to 368.3 °C, a 14.9% weight loss occurs, which can be attributed to the loss of four hydrational waters by the reaction:

$$4\text{MgCO}_3 \cdot \text{Mg(OH)}_2 \cdot 4\text{H}_2\text{O} \rightarrow 4\text{MgCO}_3 + \text{Mg(OH)}_2 + 4\text{H}_2\text{O} \quad (1)$$

According to V.R. Choudhary [21], the next two weight-loss steps are as follows:

$$4\text{MgCO}_3 + \text{Mg(OH)}_2 \rightarrow 4\text{MgCO}_3 + \text{MgO} + \text{H}_2\text{O} \quad (2)$$

$$\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2 \quad (3)$$

The corresponding mass-loss calculated from the above-mentioned equations are 3.9 and 37.8%, respectively. However, this seems not to be so with regard to our case. In the TG curve shown in Fig. 3, the second weight loss from 368.3 to 526.7 °C is 15.1%, while the third weight loss between 526.7 and 700 °C is about 25.7%. The fact that more weight-loss occurs in the second stage indicates spontaneous decomposition of Mg(OH)₂ and MgCO₃. The characteristic porous structure of the hydromagnesite sample may account for the changing of the thermal decomposition mode. A total mass loss of 55.7% is apparent, after which the residue X-rayed as MgO. The thermal effect of the sample is so small that the DTA curve only showed two weak endothermic peaks at 290.6 and 544.7 °C, respectively.

The above mentioned decomposition mechanism was confirmed by high temperature X-ray diffraction analysis. Fig. 4 shows the general view of the HTXRD patterns of hydromagnesite. From this figure it is apparent that the XRD patterns recorded at 100 and 200 °C show little difference to the pattern recorded at room temperature (Fig. 1), which is expected to be due to desorption of physically adsorbed water below 200 °C. At 300 °C, a small trace of MgCO₃ (JCPDS file number 8-479) emerges, indicating the structure disorganization of the sample while losing its crystallization water. At 400 °C, the XRD pattern exhibits an amorphous character. At this stage, the structure of the sample seriously disorganized and the decomposition of Mg(OH)₂ and some MgCO₃ took place. However, due to the thick background, no obvious diffraction peak of the resultant MgO could be found. At 500 °C, the diffraction peaks of hydromagnesite totally disappear while the pattern shows weak reflection of MgO (JCPDS file number 45-946). The diffraction peak of MgO becomes sharper at 600 °C, indicating the increasing of the crystallinity of MgO and the end of the thermal decomposition process.

Specific surface areas were determined from the nitrogen absorption data at liquid nitrogen temperature using the Brunauer–Emmett–Teller (BET) technique by means of a Micromeritics ASAP 2000 apparatus. It is found that the value of the specific surface area of the hydromagnesite sample prepared from this hydrothermal method is about 36 m² g⁻¹.

3.3. Photoluminescence study

Fig. 5a displays the photoluminescent emission of the hydromagnesite sample prepared at 100 °C for 10 h under hydrothermal conditions. The maximum emission exhibits at 448 nm when the excitation wavelength was 380 nm. With the prolonging of the reaction time, the emission of hydromagnesite becomes weak while at the same time the emission band slightly red shifted (Fig. 5a–c). In order to understand the PL enhancement, the PLE spectra of the sample were measured as well. The excitation spectra of
emission at 448, 458, and 465 nm showed that 380 nm was always the most effective excitation. This is in good agreement with the emission spectra.

3.4. The effect of reaction parameters

The reaction temperature has a significant effect on the products. Phase-pure hydromagnesite was obtained at 100°C. Above 120°C, the yield of hydromagnesite was poor and the particles were irregular. At a temperature below 80°C, no precipitate was obtained. This is due to the fact that the decomposition temperature of urea is 80°C [27], below which no CO3²⁻ could be released. Uniform and well-crystallized hydromagnesite could be obtained at the time range of 10–24 h. With the prolonging of reaction period, the crystallinity of the products increased while at the same time the pore size decreased (from the SEM observation). If the reaction time was less than 5 h, there was no precipitate.

4. Conclusion

Porous hydromagnesite with a rosette-like structure has been successfully synthesized using a convenient hydrothermal reaction at 100°C. A mechanism concerning the thermal decomposition of the product has been proposed and confirmed by in situ high temperature X-ray diffraction. The photoluminescent feature of the hydromagnesite sample was observed. This route could be expanded to the synthesis of other inorganic materials with desirable complex patterns as well as to the design of safe, inexpensive and environmentally benign optical materials.

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References