Materials Letters 120 (2014) 69–72

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Controllable fabrication of high purity $Mg(OH)_2$ nanoneedles *via* direct transformation of natural brucite

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ARTICLE INFO

Article history:
Received 31 October 2013
Accepted 9 January 2014
Available online 19 January 2014

Keywords:
$Mg(OH)_2$ nanoneedles
Nanoparticles
Direct transformation
Crystal growth
Brucite
Hydrogen bonds

ABSTRACT

High purity $Mg(OH)_2$ nanoneedles with diameters of 3–5 nm and lengths of 40–60 nm were synthesized directly from natural brucite *via* a facile and dissolution-free route in the presence of magnesium sulfosalicylate and polyethylene glycol (PEG, MW1000). Under hydrothermal conditions, magnesium sulfosalicylate caused layered brucite to disintegrate into thin nanosheets and could transport hydroxyl groups from the nanosheets to $Mg(OH)_2$ crystal nuclei as a "supplier". The PEG1000 might regulate the one-dimensional morphology and improve the purity of the $Mg(OH)_2$ nanoneedles by forming selective hydrogen bonds on the related $Mg(OH)_2$ crystal surfaces. Since this novel approach is simple and low-cost in comparison with wet precipitation method, the process can easily be scaled up.

1. Introduction

Nanostructured $Mg(OH)_2$ have attracted great attention due to their wide applications in nanodevices, nanostructured composite materials and as precursors for the synthesis of MgO [1–7]. $Mg(OH)_2$ with special morphologies, such as wire-like and needle-like nanostructures [8,9], when used as reinforcing additives in polymer matrix composites, greatly enhances the mechanical properties of these materials. High purity $Mg(OH)_2$ is also the most important precursor [1,3] for the synthesis of MgO with narrow size distribution and anticipative morphology. So far, many efforts have been focused on the synthesis of $Mg(OH)_2$ nanoneedles by controlling the wet precipitation process from Mg^{2+} solution [3,10–12]. However, to the best of our knowledge, direct fabrication of high purity $Mg(OH)_2$ nanoneedles from natural bulk brucite particles without conventional dissolution–recrystallization has not been reported until now.

In our previous studies, hexagonal and porous $Mg(OH)_2$ nanoplates have been successfully synthesized from natural brucite without dissolution procedure in the presence of specific organic molecules [13,14]. These results inspired us to investigate whether it is possible to further synthesize unique morphologies of $Mg(OH)_2$ during direct transformation from natural brucite. Herein, we demonstrate that bulk brucite undergoes a direct transformation to high purity $Mg(OH)_2$ nanoneedles under hydrothermal conditions in the presence of magnesium sulfosalicylate and polyethylene glycol (PEG) 1000. Furthermore, both of the additives can be reused many times in this process. As compared to the conventional dissolution–recrystallization methods, this novel approach is facile and low-cost when scaled up.

2. Experimental

0.3 g (0.005 M) of brucite powder (Fengcheng, China. The chemical components are given in Table S1), 0.039 g (0.0015 M) of magnesium sulfosalicylate and 0.15 g (0.0015 M) of PEG 1000 were mixed in 30 mL of deionized water, and then poured into a stainless teflon-lined autoclave (50 mL capacity). The autoclave was sealed and maintained at 160 °C for 3 h, 6 h and 12 h to obtain the reaction intermediates and 24 h to acquire the $Mg(OH)_2$ nanoneedles, respectively. The residue was collected and washed with deionized water several times. The product was then dried in a vacuum system at 50 °C for 6 h for subsequent characterization.

The structural identification was examined by X-ray diffraction (XRD) on a Rigaku D/max 2400 X-ray diffractometer using Cu Kα radiation over the range of 2θ angles from 10° to 80°. Thermal analysis was performed on a TGA/SDTA 851e thermal analyzer at a heating rate of 10 °C/min under a static atmosphere. High-resolution transmission electron microscopy (HRTEM) and the selected area electron diffraction (SAED) were used for morphological characterization of the samples. The HRTEM (Tecnai G220 instrument) was operated at an accelerating voltage of 200 kV. The $Mg(OH)_2$ content of samples was calculated by chemical titration.

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http://dx.doi.org/10.1016/j.matlet.2014.01.034

And the contents of impurities (Si, Ca and Fe) were determined by inductively coupled plasma (ICP).

3. Results and discussion

The XRD pattern of the as-prepared $Mg(OH)_2$ nanoneedles shows that all the peaks are indexed to the hexagonal $Mg(OH)_2$ phase (JCPDS no. 44-1482) (Fig. 1a), which is entirely different from natural brucite (JCPDS no. 07-0239) (Fig. S1). No peaks arising from impurities such as magnesium sulfosalicylate and PEG were detected. The IR spectra (Fig. S2) and EDX analysis (Fig. S3) suggest that sulfosalicylate and PEG were not incorporated into the final product. Moreover, the intensity ratio between reflections [001] and [110] is 1.64, which is similar to the I_{001}/I_{110} ratio (1.7) reported previously [3,11]. The high aspect ratio indicates strong growth orientation of the nanoneedles.

The TG/DTA analysis of as-synthesized $Mg(OH)_2$ nanoneedles was carried out at atmospheric conditions. As revealed in Fig. 1b, the stage of weight loss from 329 °C to 436 °C exhibits a 30.2 wt% weight loss and a corresponding derivative weight peak is observed near 396 °C. It can be clearly ascribed to the decomposition of $Mg(OH)_2$ to MgO, which is close to the theoretical weight loss of 30.8 wt% (pure $Mg(OH)_2$) [15]. It means that the contents of the main impurities of as-prepared $Mg(OH)_2$ nanoneedles (such as Si, Ca and Fe) decrease remarkably in comparison with raw brucite (Fig. S4 and Table S1). Furthermore, the titration and ICP analysis give the numerical evidence as shown in Table 1. Obviously, the purity of $Mg(OH)_2$ nanoneedles is greatly improved from 95.2 wt% (raw brucite) to 99.6 wt%.

Table 1
Titration and ICP analysis of raw brucite and $Mg(OH)_2$ nanoneedles (wt%).

Elements	$Mg(OH)_2$	Insoluble residues	Si	Ca	Fe
Raw brucite	95.1613	1.3203	0.8320	0.8004	0.1959
$Mg(OH)_2$ nanoneedles	99.5824	–	0.0098	0.0359	0.0013

The morphologies and structures of the raw material and product were examined by TEM. The natural brucite particles (Fig. 1c) are angular and irregular in shape. Interestingly, the product displays a needle-like shape with a diameter of 3–5 nm and a length of 40–60 nm (Fig. 1d), which is distinct from our previous reports ($Mg(OH)_2$ nanoplates) [13,14]. In addition, the HRTEM image reveals a perfect crystalline structure of a $Mg(OH)_2$ nanoneedle (Fig. 1e). The interplanar distance is 0.272 nm, which corresponds to the (100) planes of $Mg(OH)_2$. The SAED pattern shown in Fig. 1f can be indexed as a hexagonal crystal structure.

To investigate the formation process of $Mg(OH)_2$ nanoneedles, TEM was used to image the reaction intermediates (Fig. 2). The original close-grained natural brucite particles exhibited layered structure (Fig. 2a and Fig. S5). Subsequently, the layered particles were disintegrated into nest-like aggregation of thin nanosheets after 3 h (Fig. 2b). These nanosheets were completely disintegrated after 6 h (Fig. 2c). Finally, $Mg(OH)_2$ nanosheets transformed into nanoneedles (Fig. 2d). Additionally, the XRD patterns (Fig. S6) match the evolution process of natural brucite perfectly. In contrast, the TEM image (Fig. S7) and XRD pattern (Fig. S8) of the product prepared at room temperature and atmospheric conditions in the presence of magnesium sulfosalicylate and PEG 1000 indicate that brucite did not undergo disaggregation into thin nanosheets.

Based on the results mentioned above, a possible synthetic mechanism of $Mg(OH)_2$ nanoneedles is proposed as Fig. 3. Direct transformation from natural bulk brucite to high purity $Mg(OH)_2$ nanoneedles could circumvent the threshold of size effect [13,14,16] through a particular route which mainly involves four steps: (i) Sulfosalicylate anions firstly exchange with hydroxyl groups in the bulk phase of brucite and simultaneously insert into the interlayers of Mg^{2+} cations, which lead to the disaggregation of brucite into thin nanosheets [13,17]. (ii) Subsequently, the hydroxyl groups derived from anion exchange connect with the

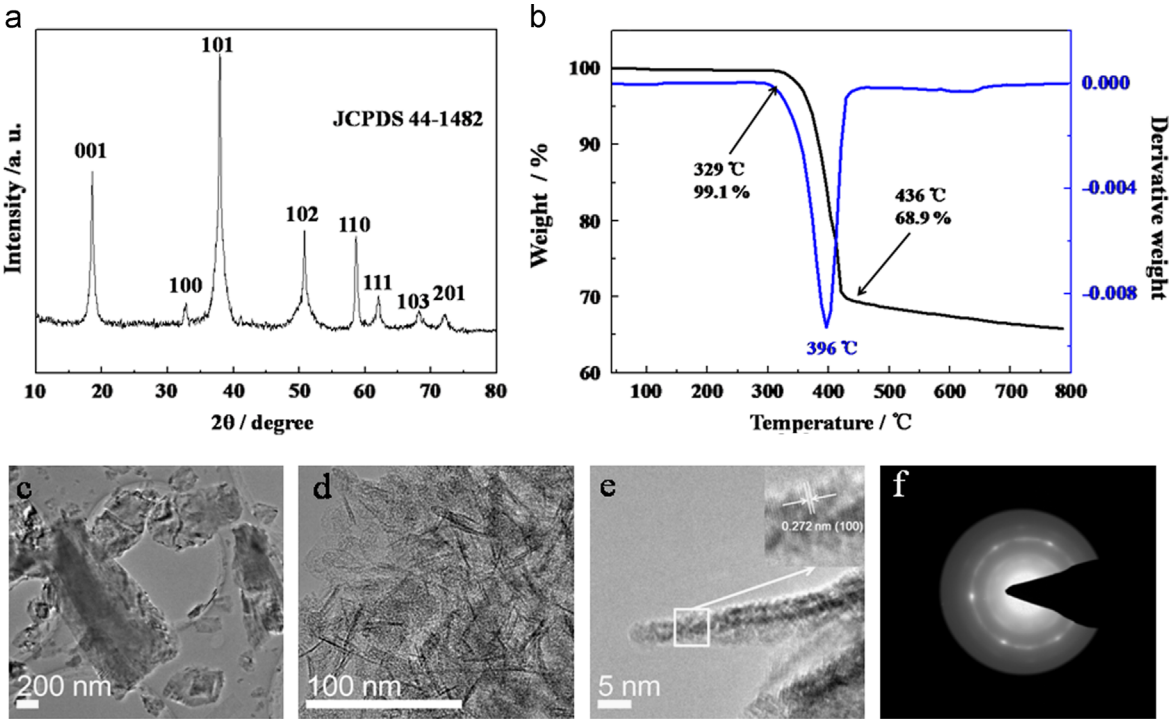

Fig. 1. (a) XRD pattern and (b) TG/DTA curves of the as-synthesized $Mg(OH)_2$ nanoneedles. TEM images of (c) natural brucite particles and (d) $Mg(OH)_2$ nanoneedles. (e) HRTEM images of $Mg(OH)_2$ nanoneedles. (f) SAED pattern of $Mg(OH)_2$ nanoneedles.