Hydrothermal Formation of the Head-to-Head Coalesced Szaibelyite MgBO₂(OH) Nanowires

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Abstract The significant effect of the feeding mode on the morphology and size distribution of the hydrothermal synthesized MgBO₂(OH) is investigated, which indicates that, slow dropping rate (0.5 drop s⁻¹) and small droplet size (0.02 mL d⁻¹) of the dropwise added NaOH solution are favorable for promoting the one-dimensional (1D) preferential growth and thus enlarging the aspect ratio of the 1D MgBO₂(OH) nanostructures. The joint effect of the low concentration of the reactants and feeding mode on the hydrothermal product results in the head-to-head coalesced MgBO₂(OH) nanowires with a length of 0.5–9.0 μm, a diameter of 20–70 nm, and an aspect ratio of 20–300 in absence of any capping reagents/surfactants or seeds.

Keywords Nanowires · Szaibelyite · Magnesium borate hydroxide · Mixing · Hydrothermal

Introduction

One-dimensional (1D) nanostructures, including nanotubes, nanorods, nanowires, and nanobelts, etc., have attracted extraordinary research interest for their multifunctionality as building blocks for bottom–up nanotechnology [6]. On the other hand, the properties of 1D nanostructure were greatly dependent on the aspect ratio [7–9], longer or higher aspect ratio has now in many cases emerged as one of the focuses of the synthesis of 1D nanostructures. As a consequence, much effort has been devoted to the synthesis of 1D nanostructures with high aspect ratio, such as capping reagents or surfactants-assisted synthesis of high-aspect-ratio hydroxyapatite [10] and CdS [11] nanorods, vanadium oxide [12] and Te [13] nanobelts, Au [14] and aluminum borate [15] nanowires; seed-mediated synthesis of high-aspect-ratio Au nanorods [16] and ZnO nanowires and nanotubes [17]; process conditions-optimized synthesis of high-aspect-ratio titanate nanofibers/nanotubes [18], Cu nanowires [19], ZnO nanorods/nanowires [20], and magnesium oxyysulfate nanowires [21].

One-dimensional nanostructured magnesium borates, including MgB₄O₇ nanowires [22], Mg₃B₂O₆ nanotubes [23] and nanobelts [24], Mg₂B₂O₅ nanowires [25, 26], nanorods [27] and whiskers [28–30], etc., have attracted much attention in recent years for their potential usage as reinforcements in the electronic ceramics [22], wide band gap semiconductors [25], antiwear additive [26], and plastics or aluminum/magnesium matrix alloys [30]. Traditionally, 1D micro-/nanostructured magnesium borates were prepared via chemical vapor deposition (CVD) [22–27] or molten salt synthesis (MSS) route [28–30] at high temperature within 850–1,250 °C or solution-based method under supercritical conditions (500–600 °C, 200–1,000 bar, 14 days) [31]. In the recent work, we developed a flux-assisted thermal conversion route to the high crystallinity pore-free Mg₂B₂O₅ nanowhiskers at a relatively low temperature as 650–700 °C [32] based on the former...
hydrothermal synthesis of MgBO₂(OH) nanowhiskers [33].

Apparently, it is of great significance to increase the aspect ratio of hydrothermally synthesized MgBO₂(OH) nanowhiskers to acquire high-aspect-ratio 1D MgₓB₂O₅ nanostructures, considering somewhat unavoidable shrinkage or breakage in the thermal conversion [34]. MgBO₂(OH) particles without morphology control were synthesized by the dissolution and phase transformation of 2MgO·2B₂O₃·MgCl₂·14H₂O at 180 °C for 72.0 h [35]. Low-aspect-ratio MgBO₂(OH) whiskers (average diameter: 30 nm, average length: 700 nm) coexisting with floccules and nanoparticles were formed by the hydrothermal reaction of MgO and B₂O₃ at 180 °C for 48.0 h [36]. Most recently, MgBO₂(OH) nanobelts have also been reported [37]. In the previous work, uniform MgBO₂(OH) nanowhiskers (diameter: 20–50 nm, length: 0.5–3 μm) were hydrothermally synthesized (240 °C, 18 h), using MgCl₂·6H₂O, H₃BO₃, and NaOH as the reactants [33].

Based on the understanding of the effect of the process parameters on the diameter, length, and aspect ratio of the hydrothermal product [38], herein we report for the first time the significant effect of the feeding mode on the morphology and size distribution of the hydrothermal product, which resulted in the head-to-head coalesced MgBO₂(OH) nanowires with a length of 0.5–9.0 μm, a diameter of 20–70 nm, and an aspect ratio of 20–300 in absence of any capping reagents/surfactants or seeds. The feeding mode-intensified 1D preferential growth was also helpful for the wet chemistry based synthesis of other 1D nanostructured materials, especially for those with anisotropic crystal structures.

Experimental

MgBO₂(OH) nanowires were synthesized by a modified coprecipitation at room temperature followed by the hydrothermal treatment. In a typical procedure, 4 mol L⁻¹ of NaOH was dropped into the solution containing 3 mol L⁻¹ of H₃BO₃ and 2 mol L⁻¹ of MgCl₂ under vigorous magnetic stirring at room temperature, keeping the molar ratio of Mg:B:Na as 2:3:4. Thereafter, 40 mL of the slurry (MgₓB₄O₁₃·7H₂O) [33] was put into a Teflon-lined stainless steel autoclave with a capacity of 70 mL. The autoclave was heated to 240 °C and kept under isothermal condition for 18.0 h, and then cooled down to room temperature naturally. The product was filtered, washed with deionized water for three times and dried in vacuum at 105 °C for 6.0 h. All of the reactants were analytical grade without further purification. To investigate the hydrothermal formation of the MgBO₂(OH) nanowires, the dropping rate, droplet size, and amount of the NaOH solution and also the hydrothermal time were adjusted within the range of 0.5–1.0 drop per second (d s⁻¹ hereafter), 0.02–0.12 mL per drop (mL d⁻¹ hereafter), 3.5–7.0 mL, 2.0–18.0 h, respectively, whereas with other conditions kept the same.

The composition and structure of the samples were identified by an X-ray powder diffractometer (XRD, D/max-RB, Rigaku, Japan) using CuKα radiation (λ = 1.54178 Å). The morphology of the samples was examined with a field emission scanning electron microscopy (FESEM, JSM 7401F, JEOL, Japan) and a high resolution transmission electron microscopy (HRTEM, JEM-2010, JEOL, Japan). The particle size of that contained in the precursor slurry was detected via a malvern particle size analyzer (MICRO-PLUS, MALVERN, England). And the average diameter and length of the hydrothermal product were estimated by direct measuring about 200 particles from the typical FESEM images taken at 1.0 kV with the magnifications of 15,000–40,000.

Results and Discussion

According to the analysis of the precipitate obtained at room temperature [33], the corresponding coprecipitation leading to the slurry containing white precipitate Mg₇B₄O₁₃·7H₂O can be written in ionic form as follows:

\[ \text{H}_3\text{BO}_3 (s) + \text{H}_2\text{O} \rightarrow \text{B(OH)}_4^- (aq.) + \text{H}^+ (aq.), \]

\[ \text{MgCl}_2 (aq.) \rightarrow \text{Mg}^{2+} (aq.) + 2\text{Cl}^- (aq.), \]

\[ \text{NaOH} (aq.) \rightarrow \text{Na}^+ (aq.) + \text{OH}^- (aq.), \]

\[ 4\text{B(OH)}_4^- (aq.) + 7\text{Mg}^{2+} (aq.) + 10\text{OH}^- (aq.) \]

\[ \rightarrow \text{Mg}_7\text{B}_4\text{O}_{13} \cdot 7\text{H}_2\text{O} (s) + 6\text{H}_2\text{O}. \]

The hydrothermal conversion can thus be expressed as follows, definitely showing the necessary basic medium for the hydrothermal formation of szaibelyite MgBO₂(OH) phase [39]:

\[ \text{Mg}_7\text{B}_4\text{O}_{13} \cdot 7\text{H}_2\text{O} (s) + 3\text{B(OH)}_4^- (aq.) \]

\[ \rightarrow 7\text{MgBO}_2\text{(OH)}(s) + 3\text{OH}^- (aq.) + 8\text{H}_2\text{O}. \]
decreased within the range of 0.12–0.02 mL d\(^{-1}\) (Fig. 1e–h). It was worth noting that, the morphology uniformity was greatly improved with the slowing down of the dropping rate from 1.0 to 0.5 d s\(^{-1}\) under the same droplet size, denoted as Fig. 1a, e, b, and f, etc. Most significantly, the uniform MgBO\(_2\)(OH) nanowhiskers (Fig. 1h) were obtained while the dropping rate and droplet size were kept as 0.5 d s\(^{-1}\) and 0.02 mL d\(^{-1}\), respectively, indicating the promotion of the morphology uniformity via the slow dropping rate and small droplet size of the dropwise added NaOH solution.

Size variation of the hydrothermal product with the droplet size of the NaOH solution showed that the average length and diameter of the hydrothermal product derived from dropping rate of 0.5 and 1.0 d s\(^{-1}\) both decreased slightly with the decrease of the droplet size from 0.12 to 0.07 mL d\(^{-1}\), which however both began to increase when the droplet size further decrease from 0.05 to 0.02 mL d\(^{-1}\) (Fig. 2a–b). Meanwhile, within the same range of the droplet size as 0.02–0.05 mL d\(^{-1}\), the average length and diameter of the hydrothermal product increased with the decrease of the dropping rate from 1.00 to 0.5 d s\(^{-1}\). The specific evolution trend of the average length and diameter of the hydrothermal product (Fig. 2a–b) determined the corresponding change of the average aspect ratio of the hydrothermal product with the dropping rate and droplet size within the range of 0.02–0.05 mL d\(^{-1}\).

The effect of the feeding mode on the hydrothermal product indicated that slow dropping rate (0.5 d s\(^{-1}\)) and small droplet size (0.02 mL d\(^{-1}\)) of the dropwise added NaOH solution were favorable for enlarging the aspect ratio of the hydrothermal product thus could promote the 1D growth of the MgBO\(_2\)(OH) nanostructures during the subsequent hydrothermal treatment. Since low concentration of the reactants, relatively long reaction time and high temperature favored the synthesis of MgBO\(_2\)(OH) nanowhiskers with a longer size and higher aspect ratio [38], less amount of NaOH solution (4 mol L\(^{-1}\)), in other words, lower initial concentration of NaOH (0.17 mol L\(^{-1}\)) was employed in the room temperature coprecipitation so as to further increase the length and aspect ratio of the hydrothermal product, with the molar ratio of Mg:B:Na and also total volume of the mixed solution unchanged. The resultant well dispersed uniform nanowires (Fig. 3a) with high
crystallinity (Fig. 3b, b₁–b₂) were obtained, which consisted of pure phase of monoclinic MgBO₂(OH) (PDF No. 39-1370) as shown in Fig. 3c. The interplanar spacings of 0.597 nm detected from the legible lattice fringes along the axis of the nanowire (Fig. 3b₁) was quite similar to that of the (200) planes of the standard MgBO₂(OH), indicating the preferential growth direction of the nanowires parallel to the (200) planes, in agreement with that of the MgBO₂(OH) nanowhiskers along the c-axis [38] and also the growth habit of the natural szabelyite (MgBO₂(OH)) [40]. The statistic data showed that the MgBO₂(OH) nanowires had a length of 0.5–9.0 µm (approx. 80% within 1–5 µm), a diameter of 20–70 nm (approx. 68% within 30–50 nm), and an aspect ratio of 20–300 (approx. 78% within 20–100) (Fig. 3d–f). Apparently, the length and aspect ratio of the resultant MgBO₂(OH) nanowires were much higher than those of the MgBO₂(OH) nanowhiskers [33].

To investigate the formation of the nanowires, the morphology evolution of the hydrothermal products acquired at 240 °C for various time were tracked (Fig. 4a–c), in case of slow dropping rate (0.5 d s⁻¹), small droplet size (0.02 mL d⁻¹), and low initial concentration of the NaOH (0.17 mol L⁻¹) during the room temperature coprecipitation. Short and thin nanowhiskers having grown for 2.0 h (Fig. 4a) tended to be attached with each other either head-to-head or side-by-side (denoted as dotted circles), and the nanowhiskers became longer with fewer attached phenomena observed as the time prolonged to 6.0 h (Fig. 4b). Finally, MgBO₂(OH) nanowires with high aspect ratio and sometimes curved 1D morphology were obtained when hydrothermally treated for 18.0 h, owing to the previous head-to-head or side-by-side attachment growth of the individual nanowhiskers (Fig. 4c). Further, TEM observations on the joint sections of the nanowires indicated that, either the seemingly straight nanowires (Fig. 4 d₁–d₂) or curved ones (Fig. 4 d₃–d₄) were formed via the head-to-head overlapped or side-by-side attached growth of the nanowhiskers. Particularly, the legible lattice fringes parallel to the axis of the nanowire (Fig. 4e₁–e₂) with the detected interplanar spacings of 0.597 nm revealed that the MgBO₂(OH) nanowires tended to be attached with one other in a direction approx. along the (200) planes, leading to the seemingly straight or slightly curved nanowires.

The formation of the MgBO₂(OH) nanowires could thus be depicted, as shown in Fig. 5. Tiny amorphous irregular Mg₂B₄O₁₃·7H₂O [33] nanoparticles derived from the coprecipitation at room temperature with small droplet size and slow dropping rate of the dropwise added NaOH solution gradually dissolved and further converted to short and thin crystalline 1D MgBO₂(OH) nanostructures (i.e., nanowhiskers) with the hydrothermal temperature continuously increased to 240 °C. With time going on under the isothermal condition (240 °C), short and thin MgBO₂(OH) nanowhiskers began head-to-head overlapped or side-by-side attached growth, due to the necessity of reducing the
whole surface energy especially on the newly grown tip position to promote the stability of the entire system. And the overlapped 1D nanostructures finally grew into the head-to-head coalesced MgBO$_2$(OH) nanowires with relatively smooth surface and uniform diameter along the axis when hydrothermally treated at 240°C for 18.0 h. During the early phase conversion of Mg$_7$B$_4$O$_{13}$·7H$_2$O and original formation of the 1D MgBO$_2$(OH), the special chain-like structure units existed in the bulk crystal structure of szalibelyite [40] should be considered. The distorted Mg–O octahedra share edges to form a chain with two octahedra in width parallel to the c-axis, two such nonequivalent chains share corners to form a sheet parallel to (200) planes, and the sheets are further held together by the pyroborate ions [B$_2$O$_4$(OH)]$^{3-}$. The specific anisotropic crystal structure was believed to be responsible for the formation of the original 1D MgBO$_2$(OH) nanostructures. On the other hand, the late growth of the overlapped 1D MgBO$_2$(OH) nanostructures into the coalesced nanowires might be attributed to the joint effect of the oriented attachment [41–43] and Ostwald ripening [44, 45], which however needed further in-depth investigation.

Comparatively, head-to-head overlapped or side-by-side attached growth phenomena were not readily observed in the morphology evolution of the hydrothermal products obtained at 240 °C for various time originated from the room temperature coprecipitation in case of relatively big droplet size and fast dropping rate of the NaOH solution [38]. Thus, the droplet size and dropping rate of the dropwise added NaOH solution played a key role in the formation of the small size nanoparticles of the hydrothermal precursor (slurry containing Mg$_7$B$_4$O$_{13}$·7H$_2$O) and
further formation of the high aspect ratio hydrothermal product. Small droplet size and slow dropping rate under vigorous stirring are favorable for the creation of the low supersaturation, which favors the 1D preferential growth of the nanocrystals with anisotropic crystal structures [5, 21], similar to the double-injection method for the synthesis of magnesium oxysulfate nanowires [21]. Consequently, the low supersaturation originated from the room temperature coprecipitation in case of small droplet size and slow dropping rate of the dropwise added NaOH solution promoted the formation of the small size precursor particles and further formation of the short and thin MgBO$_2$(OH)
nanowhiskers, resulting in subsequent head-to-head overlapped or side-by-side attached growth and finally head-to-head coalesced MgBO$_2$(OH) nanowires. However, the extended experiments showed that, with other conditions kept the same, longer hydrothermal time such as 30.0 h was not favorable for the formation of longer MgBO$_2$(OH) nanowires, which led to broad leaf-like MgBO$_2$(OH) nanostructures with distinct wide distribution of the diameter due to excess side-by-side attached growth [39]. Moreover, unlike some other nanowires synthesized in presence of capping reagents or surfactants [5], MgBO$_2$(OH) nanowires were obtained in absence of any surfactants, and neither hexadecyl trimethyl ammonium bromide (CTAB) nor sodium dodecyl benzene sulfonate (SDBS) have been proved effective for the formation of high aspect ratio MgBO$_2$(OH) nanowhiskers.

Conclusion

In summary, the significant effect of the feeding mode on the morphology and size distribution of the hydrothermal synthesized MgBO$_2$(OH) indicated that, slow dropping rate (0.5 d s$^{-1}$) and small droplet size (0.02 mL d$^{-1}$) of the dropwise added NaOH solution were favorable for promoting the 1D preferential growth and thus enlarging the aspect ratio of the 1D MgBO$_2$(OH) nanostructures. The joint effect of the low concentration of the reactants and feeding mode resulted in the head-to-head coalesced MgBO$_2$(OH) nanowires with a length of 0.5–9.0 μm, a diameter of 20–70 nm, and an aspect ratio of 20–300 in absence of any capping reagents/surfactants or seeds. The feeding mode-promoted 1D preferential growth was also helpful for the wet chemistry based synthesis of other 1D nanostructured materials, especially for those with anisotropic crystal structures.

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