Facile synthesis of zinc hydroxyfluoride nanobelts and effect of hexamethylenetetramine for growth direction

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ABSTRACT

Control of nanomaterial morphology has been investigated to utilize for the desired application. 1D nanomaterials are ideal for various applications because of their excellent carrier transportability and huge specific surface area. Due to their advantages, various methods have been developed to grow in a specific direction. Herein, we introduced a simple synthesis method of freestanding Zinc hydroxidefluoride (ZnOHF) nanobelt as 1D material without seed or substrate using aqueous solutions. The ZnOHF nanobelt was synthesized using zinc fluoride and hexamethylenetetramine (HMT) at 80°C for 3 h. Even though low synthesis temperature, ZnOHF demonstrated good crystallinity and a homogeneous nanobelt structure. The ZnOHF nanobelts were grown over several μm to <010> direction with less than 100 nm width. In addition, the growth direction of the nanobelt was controlled by the concentration of HMT. The width of the nanobelt was broader by a decrease in HMT concentration. It was considered that crystal nucleation and growth of ZnOHF could be influenced by OH⁻ and NH₄⁺ ions generated from HMT decomposition.

1. Introduction

Nanomaterials have been widely utilized for gas sensing applications due to their advantages based on size. The extremely tiny size of particles leads to numerous grain boundaries. When the boundaries are exposed to oxygen in an excited state by heat or UV, they become the depletion layers that are important factors for gas sensing [1]. Additionally, the large specific surface area of nanomaterial helps to enhance the gas sensing performance [2]. However, excessively increasing the number of the boundary has the opposite effect on gas sensing since electron transfer for catalysis reaction is equally important. Therefore, suitable morphology of nanomaterial has been investigated and fabrication of nanomaterial has received considerable attention. As a result, various dimensions such as nanoparticles (0D), nanowire (1D), and nanosheet (2D) were developed [3–8]. Among them, 1D nanomaterial has been focused on due to its anisotropic crystal structures. Because its carrier transport efficiency is better than 0D nanomaterial using contact particles as the pathway through grain boundaries. In addition, the specific surface area is larger than the 2D nanomaterial. The transport efficiency is enhanced due to oriented electronic/ionic transport channels along their growth direction and multiple junctions as transport sites [9]. And stacked
1D material makes numerous voids except for junctions. Despite these advantages, the formation of 1D material is complicated that required a substrate or seed to control the growth direction [10–12]. Therefore, a simple synthesis method for free-standing 1D materials becomes a promising research topic.

Zinc hydroxide fluoride (ZnOHF) is an important zinc-containing material. It has been used as a catalyst for pyridine formation and as a precursor for ZnO production [13]. In addition, it was utilized as base material for ZnO with atomic steps for ultra-sensitive gas sensors [14]. However, the synthesis method of ZnOHF nanomaterial was rarely reported and their morphology was micrometer scale in previous. In addition, most of the synthesis methods were hydrothermal methods over 100°C and prepared samples usually showed aggregated morphology. In previous results, nanowire structures were observed at the edges, but they were not separated from each other, and it seems to be grown from the center as nuclei [15]. Even the same material, overall morphology is significant to utilize for practical applications. In order to maximize the advantages of the 1D material, we developed a synthesis method of nanobelt-shaped ZnOHF without any aggregation. Furthermore, the influence of the reactant ratio between zinc fluoride and hexamethylenetetramine (HMT) was investigated. During the synthesis process, the HMT provides OH\(^-\) ions by reaction with H\(_2\)O [16,17]. Due to this reason, HMT is widely used for the synthesis of metal oxides such as SnO\(_2\), ZnO, and NiO, and their crystal growth progress was affected by HMT concentration [18–20]. It could be considered that the crystal growth of ZnOHF could be influenced by HMT as same as other metal oxides. Thus, we investigated the effect of HMT on the ZnOHF growth.

2. Experimental procedure

2.1. Fabrication of ZnOHF nanobelt

ZnF\(_2\)·4H\(_2\)O (10 mM) and HMT (10, 5, 2.5, 1.25 mM) were dissolved in 200 mL of distilled water at 80°C. The solution was kept at 80°C for 3 h in the oven. The white powder was collected by centrifugation, washed with ethanol, and then dried at 80°C.

2.2. Characterization techniques

Field-emission scanning electron microscopy (FE-SEM, JSM-6335FM, JEOL) and transmission electron microscopy (TEM, Tecnai Osiris, FEI) were performed to confirm the nanobelt structure. The crystal structure of the samples was revealed via X-ray diffraction (XRD, SmartLab, Rigaku) with Cu Ka (\(\lambda = 1.5418 \text{ Å}\)) radiation, at 40 kV and 30 mA. The chemical state of the surface was investigated through X-ray photoelectron spectroscopy (XPS, ESCA 3400, Shimadzu). N\(_2\) adsorption/desorption isotherms were obtained at 77 K with cooling by liquid nitrogen using a surface area analyzer (Nova 2200e, Quantachrome Instruments). The specific surface area was determined by the Brunauer–Emmett–Teller (BET) method. The pH of the solution was measured by pH meter (Seven Easy S20, Mettler Toledo). The crystal structure models were produced using the VESTA program [21].

3. Results and discussion

FE–SEM and TEM measurements were carried out to examine the morphology of the ZnOHF nanobelt. Fabrication of ultra-long and thin structures as 1D material by the simple and moderate method was confirmed. Figure 1a) shows plenty of nanobelt structures in micrometer scaled length. The length was strongly related to the synthesis temperature as shown in Figure 5). The ZnOHF which was fabricated at 70°C exhibited a relatively short length. The width of the nanobelt was under 100 nm and these are thin enough that other structures can be seen through in the TEM image (Figure 1b)). As shown in the Figure 1c), the growth orientation of ZnOHF was <010> direction (b-axis) according to the corresponding selected area electron diffraction (SAED) pattern. A detailed chemical analysis was carried out using high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) and EDS elemental mappings. In the elemental mapping results, Zn (31.99 at.%), O (34.54 at.%), and F (33.47 at.%) were uniformly distributed in the ZnOHF. The EDS elemental composition is well matched to the general elemental composition of the ZnOHF structure.

The crystal structure of ZnOHF was revealed by the XRD result. As shown in Figure 2a), the diffraction pattern was found to match the orthorhombic structure Pnna (JCPDS No. 01–076-7466). The observed peaks at 2\(\theta\) = 20.7°, 32.3°, 35.6°, and 51.8° were indexed to the (110), (310), (111), and (221) planes of the ZnOHF phase, respectively. The unit cell of ZnOHF was presented in Figure 2b and its projection images for ac and ab planes were illustrated in Figure 2c,d). Based on the crystal information, the formation process of the ZnOHF nanobelt could be predicted. In this study, ZnF\(_2\) and HMT were used to construct the ZnOHF structure in aqueous solutions. The ZnF\(_2\) was used for the resource of Zn and F atoms (Equation 1) and HMT (C\(_8\)H\(_{12}\)N\(_4\)) was consumed to serve OH\(^-\) ions. In the case of HMT, it reacts with water molecules at high temperatures resulting in the production of OH\(^-\) ion in two ways. The first way is NH\(_3\) generated from HMT, after that NH\(_3\) reacts again with the water molecule. As the
result, NH$_4^+$ ions and OH$^-$ ions are formed (Equations 2–3) [22]. Another way is HMT-4 H$^+$ cationic formation by HMT and water molecule reaction and OH$^-$ ion was produced in this case (Equation 4) [23]. These OH$^-$ ions may play an important role in the formation of ZnOHF and the expected formation route is as follows:

\[
\text{ZnF}_2 \rightarrow \text{Zn}^{2+} + 2\text{F}^- \quad (1)
\]

\[
\text{C}_6\text{H}_{12}\text{N}_4 + 6\text{H}_2\text{O} \rightarrow 6\text{HCHO} + 4\text{NH}_3 \quad (2)
\]

\[
\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^- \quad (3)
\]

\[
\text{C}_6\text{H}_{12}\text{N}_4 + 4\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{N}_4 - 4\text{H}^+ + 4\text{OH}^- \quad (4)
\]
Figure 3. a) High-resolution XPS spectra of Zn2p, O1s, and F1s and c) specific surface area for the ZnOHF nanobelts.

\[
\text{Zn}^{2+} + \text{F}^- + \text{OH}^- \rightarrow \text{ZnOHF} \quad (5)
\]

XPS spectra analyses were conducted to reveal the chemical bonding information in Figure 3a. In the high-resolution scan of the Zn2p spectrum, two peaks associated with 2p3/2 and 2p1/2 were observed at 1022.6 eV and 1045.7 eV, respectively. The O1s spectra appeared at 534.1 eV and the peak position was shifted as compared with the typical O peak related to OH (531 – 532 eV) in hydroxide [24]. It is a chemical shift owing to the F atom that has strong electronegativity. The peak associated with F1s was observed at 687.5 eV. The specific surface area of the nanobelt structures was characterized by the N\textsubscript{2} adsorption/desorption isotherms. The calculated BET surface areas for the ZnOHF nanobelt were 230.96 m\textsuperscript{2}g\textsuperscript{-1}. The surface area of our sample prepared by the simple synthesis method was quite larger than that previously reported ZnOHF (Table S1) [13,15,25,26].

We found the synthesis way for ZnOHF nanobelt as a 1D material and confirmed its crystal information, preferred growth direction, surface chemical bonding information, and specific surface area. In addition, it was confirmed that HMT plays an important role during ZnOHF formation progress by serving OH\textsuperscript{-} ions. Therefore, it was considered that ZnOHF nanobelt morphology could be controlled by HMT concentration. Morphology control technology according to the purpose is a significant technique in the nanomaterial research field. Therefore, it is necessary to investigate the shape change by the HMT concentration. The ZnOHF nanobelt samples were synthesized with various HMT concentration and each HMT/ZnF\textsubscript{2} molar ratio were 1, 1/2, 1/4, and 1/8. The notable point according to the change of HMT concentration was a variation of width as shown in Figure 4. The maximum width of ZnOHF increased as decreasing of HMT/ZnF\textsubscript{2} molar ratio. The maximum width was 59, 104, 147, and 338 nm when the HMT/ZnF\textsubscript{2} molar ratio was 1, 1/2, 1/4, and 1/8, respectively.

As mentioned in Equations 2–4, HMT is decomposed to OH\textsuperscript{-}, HMT-4 H\textsuperscript{+}, and NH\textsubscript{4}\textsuperscript{+} in hot water. Thus, pH measurement can be indirectly informed the amounts of generated ions not only OH\textsuperscript{-} during heat decomposition. Figure 5a) shows the pH of the solution that mixed only HMT and water and heated at 80°C for 3 h. The result shows how much the amount of OH\textsuperscript{-} is generated during ZnOHF synthesis depending on the amount of HMT. As compared with Figure 5b) which showed the maximum width of ZnOHF, pH clearly demonstrates an inverse proportion. These results indicated that the crystal growth direction could be controlled by HMT, especially generated

Figure 4. a-d) SEM images of ZnOHF nanobelt synthesized by different HMT/ZnF\textsubscript{2} molar ratios. e-h) its maximum width of nanobelt structure.
cations from it. According to the SAED pattern (Figure 1c), the ZnOHF nanobelt as a 1D anisotropic structure was formed along the b-axis. And crystal growth along to a-axis is associated with the width of the nanobelt based on the crystallographic images (Figure 2c,d). Therefore, a narrowing of width at high pH conditions might be due to a prohibition of width expansion by generated cations from HMT. As presented in Figure 2c, OH is located at the outermost of the ZnOHF unit cell in the a-axis direction. Thus, the adsorption of positive ions could limit the growth of material along the a-axis. During the HMT decomposition, HMT-4 H\(^+\) cationic and NH\(_4\)\(^+\) are generated and these positive ions can prohibit the growth forward to the a-axis.

XRD results of ZnOHF synthesized with various HMT/ZnF\(_2\) molar ratios supported our hypothesis. With varying HMT concentrations, overall peak positions were similar and the intensity ratio between the peak was not reversed as shown in Figure 6a). It was due to the nanobelt structure of ZnOHF would not be changed by the change in HMT concentration. However, some peaks indicated a prohibition of crystal growth along to a-axis as increasing HMT. Increasing peak intensity of (400) at 35.07° was obviously observed as compared with (111) by decreasing HMT. In addition, (601) peak (62.02°) emerged at a relatively low HMT concentration.

4. Conclusions
Freestanding ZnOHF nanobelt was successfully synthesized by the low-temperature aqueous solutions synthesis method. The nanobelt structure as 1D nanomaterial was simply prepared without any seed or template. It has several micrometers in length meanwhile the width was less than 100 nm. The SAED pattern indicated that the nanobelt structure was grown along the b-axis. The maximum width of ZnOHF was controlled by HMT concentration and it was due to the difference of OH\(^-\) ions amount from HMT by heat decomposition. For utilizing applications, the fabrication of a much thinner nanobelt is required to maximize the catalytic effect. In this study, the optimal synthesis condition was a 1:1 molar ratio of ZnF\(_2\) and HMT, showing the thinnest width of 59 nm. In

Figure 5. a) pH of HMT aqueous solution with different concentrations and b) maximum width of ZnOHF nanobelt synthesize with different HMT concentrations.

Figure 6. a) the diffraction pattern of ZnOHF nanobelt synthesized by various HMT concentrations, b) variation of peak intensity ratio according to HMT concentration.
conclusion, the role of HMT in the ZnOHF synthesis process can be understood and the technology of growth control on nanostructure would play an important role in improving the performance of nanomaterial applications.

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