A novel synthesis of nanoflower-like zinc borate from zinc oxide at room temperature

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Abstract
For the first time, the nanoflower-like zinc borate compound was obtained by precipitation at room temperature using zinc oxide nanoparticles as a precursor. The obtained zinc borates were characterized by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), x-ray diffraction (XRD), thermal gravimetric analysis (TGA), and Raman spectroscopy analysis. Monoclinic of zinc borate $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$ was achieved under the XRD pattern and the elemental chemical analysis. The particle size of the obtained materials is approximately 5 nm using TEM analysis. The TGA shows that the achieved zinc borate is outstanding stable at high temperatures. The result of this work provides a new route for the fabrication of zinc borate nanoparticle, which could be widely used in many applications.

Introduction
Zinc borate compound is a commercial material of significant interest that is commonly used in many different fields such as paints, plastic, rubber, ceramics, wood applications due to its abundance, high thermal stability and non-toxicity [1–5]. Besides, zinc borate is an important inorganic compound that is commonly used in fire-retardant materials [6, 7]. In some applications, zinc borate is used as an industrial pigment, an additive in coating owing to the smoke suppressing properties [8, 9].

Because of their significance use in diverse industrial applications, in recent years, many research groups have focused on the synthesis method to produce zinc borate from a variety of precursors and using different methodologies. The obtained zinc borate has a generally micro size. For example, Gao et al synthesized zinc borate compound using $\text{H}_2\text{BO}_3$ and zinc sulfate $\text{ZnSO}_4$ at room temperature, but it took several days to obtain the full precipitation of zinc borate. The particle size value was missed, but its XRD pattern shows that the size of the synthesized zinc borate could be up to several microns [8]. Acarali et al [9] have fabricated zinc borate from zinc oxide and acid boric in the presence of modifying agents such as propylene glycol, kerosene, oleic acid. The synthesis condition was carried out at the temperature from 50 to 120 °C for several hours. During the synthesis, phosphate ester was used as a modifying agent. The synthesized zinc borate nanowhiskers present a monoclinic crystal with 50–100 nm of particle size [10]. In addition, zinc borate nanowhiskers were also fabricated by using seed crystals. The average size of the obtained zinc borates is from 4 to 16.6 μm.

However, the diffusion of zinc borate particles with micro-size in the polymeric matrix is quite problematic, which can limit their use in many applications. Therefore, it is necessary to fabrication zinc borate in the nanosize for the diffusion purpose in many matrices. In recent years, extensive studies have been reported to obtain the nanoparticles of zinc borate. Chen et al reported the synthesis of nano-flake like zinc borate by a co-precipitation method using ammonia, zinc nitrate, and borax as precursors. The precipitation method was carried out by forming a complex solution of zinc ions with ammonia in the presence of borax. The synthesis was performed at 45 °C for several hours. The obtained material has a size of around 200 nm of particle size [11]. Zheng et al also have reported the one-step precipitation of zinc borate nanowhiskers using sodium borate and zinc nitrate. The synthesis condition was carried out at 70 °C for 11 h for the complete precipitation. During the synthesis, phosphate ester was used as a modifying agent. The synthesized zinc borate nanowhiskers are recorded as a monoclinic crystal with 50–100 nm of particle size [12].
synthesized using dodecylbenzene sulfonate as a surfactant by Gao. The synthesis was carried out at the temperature of 50 to 90 °C for 7 h, which exhibited nanowhiskers with particle sizes from 50 to 100 nm. Hexadecyl trimethyl ammonium bromide (CTAB) was used as a modifying agent for the synthesis of nanosphere-like zinc borate. The synthesis was carried out at 70 °C for 7 h as other methodologies. The author reported that the size of the nanosphere is also around 50–100 nm [13].

Various techniques have been used so far for the synthesis of zinc borate nanostructures [14–17]. However, most of them require temperature [3], modifying agents [16, 18–20], template [17], which may lead to the high-cost problems. The obtained nanoparticles are still large; it seems very difficult to get the nanoparticles with the size smaller than 20 nm.

In this work, for the first time, nanoflower-like of zinc borate was one-step synthesized at room temperature using nanoparticle of ZnO as a precursor. The particle size of the achieved materials was carried out by TEM and FEG-SEM analysis. The result provides a new route for the fabrication of zinc borate nanoparticle, which could be widely used in many applications.

Experimental section

Materials

All chemical reagents in the synthesis process of this experiment, namely, Zn(COOH)2·3H2O (99.5 wt% purity), (NH2)2CO (99,2 wt% purity), H3BO3 (99,2 wt% purity), came from Merck Chemicals.

The synthesis of zinc oxide ZnO nanoparticles

The synthesis of ZnO nanoparticles was performed following the method of Vu et al [21]. In a typical synthesis, an aqueous solution of zinc acetate 0.05 M was prepared in 100 ml distilled water. Consequently, urea was added to the concentration of 1 M under magnetical stirring. The pH of the solution was adjusted to 4.0, using several drops of concentrated acetic acid. Then the mixture was hydrothermally treated at 80 °C for 12 h at a constant temperature. Finally, the precipitated Zn(OH)2 was thoroughly washed with distilled water and dried in an oven at 60 °C for several hours. The ZnO nanoparticles were obtained after the calcination step at 250 °C for 1 h in the air.

The synthesis of nanoflower-like zinc borate nanoparticles

The fabrication of nanoflower-like zinc borate was done using the ZnO nanoparticles as the primary precursor with only one-step precipitation method. In a typical synthesis, boric acid H3BO3 and ZnO nanoparticles were mixed in 200 ml of distilled water. The molar ratio between H3BO3 and ZnO is varied from 1 to 5. The mixture was stirred at a constant room- temperature to obtain the complete precipitation of zinc borate. The synthesis time was varied from 3 to 6 h. After the reaction, the white slurry zinc borate was vacuum filtered and thoroughly washed by distilled water for several times. Finally, the achieved zinc borate particles were dried in the oven at 50 °C for 15 h.

The determination of zinc oxide in the solid sample

Zinc oxide was determined in solid samples by the EDTA titration. In a typical titration, 5 mL of HCl 37% was used to dissolve 0.15 g samples. Consequently, the pH of the solution was adjusted to 9.0, using NH3 28%. Then the solution was titrated by EDTA using the Erichrome black T indicator. The following formula calculates the zinc oxide content in the zinc borate sample:

\[
\%\text{ZnO} = \frac{V_{\text{EDTA}}}{m} \times 0.004069
\]

Where:

\( V_{\text{EDTA}} \) is the volume of EDTA, ml
\( m \) is mass of zinc borate, g

Determination of B2O3 in the zinc borate

0.15 g of the solid sample was dissolved in 5 mL HCl 37%. An excess volume of EDTA was added to eliminate the amount of zinc ion in the solution. Therefore, the solution was titrated by using NaOH 1 M to adjust the pH to 7. The following formula calculates the B2O3 amount of the zinc borate sample:

\[
\%\text{B}_2\text{O}_3 = 0.348101 \times \frac{V_{\text{NaOH}}}{m} \times 1
\]

Where:
Material characterization

The x-ray diffraction (XRD) patterns of the sample were recorded on Bruker D8 Advance instrument operating at 40 kv and 40 mA using Cu Kα radiation (λ = 0.15406 nm). The scanning electron microscopy (SEM, FEI Quanta FEG 650 model) and transmission electron microscopy (JEOL- JEM 1010 Transmission Electron Microscope 300 kV) were used to examine the morphology of the samples. The instrumental contribution to line broadening was considered. The micro–Raman spectrophotometer (JASCO Raman NRS-3000) was used to record the Raman spectra. An excited laser at 633 nm was used for the spectra recording at room temperature. The functional groups on the surface were characterized by Fourier transform infrared (FT-IR) spectroscopy (FT-IR 8400 s Shimadzu) from KBr pellets at a range of 400–4000 cm⁻¹. The thermal gravimetric analysis was performed on a USA SDT 2960 TA Instruments;

Results and discussion

Effect of synthesis conditions on obtained products specification

The synthesis conditions employed are the key to the controlling of yield production, morphology, and crystallinity of zinc borate obtained. It is necessary to maximize the synthesis yield, and also to optimize the particle size, as well as to promote the homogenous dispersion of the zinc borate in a polymer matrix due to the several prospective applications of zinc borate [1, 10].

The variables synthesis conditions of zinc borate were described in table 1. The obtained zinc borate was analyzed for the ZnO and B₂O₃ contents and the synthesis reaction synthesis. All the results were listed in table 2. When the molar ratio between H₃BO₃: ZnO is lower than 3, the ZnO content is much higher than that of B₂O₃ content. This phenomenon illustrates that there is an incomplete conversion of zinc oxide into zinc borate [10]. When the molar ratio between H₃BO₃: ZnO is equal to or higher than 3, the ZnO content is lower than that of B₂O₃ content. The results indicate that there is a complete conversion of zinc oxide into zinc borate. Furthermore, when the molar ratio between H₃BO₃: ZnO is equal to 3 and the reaction time is up to 4 h, there is a complete conversion of zinc oxide into zinc borate, and the reaction yield is achieved by 98%.

From the variables employed in table 1 and the yield and composition date in table 2, it can conclude that the best synthesis condition of zinc borate is as follows:

1. The molar ratio between H₃BO₃: ZnO is 3
2. The optimum synthesis time is 4 h.

Table 1. Variables employed in this work for the synthesis of zinc borate.

|          | ZnB1 | ZnB2 | ZnB3 | ZnB4 | ZnB5 | ZnB6 | ZnB7 | ZnB8 | ZnB9 |
|----------|------|------|------|------|------|------|------|------|------|
| (H₃BO₃:ZnO) | 1    | 2    | 3    | 4    | 5    | 3    | 3    | 3    | 3    |
| Time synthesis, h | 4    | 4    | 4    | 4    | 4    | 3    | 4    | 5    | 6    |

Table 2. Specifications of the obtained zinc borates from different experimental conditions.

|          | % Yield | % ZnO | %B₂O₃ | %H₂O | Zinc borate (xZnO.yB₂O₃.zH₂O) |
|----------|---------|-------|-------|------|-------------------------------|
| ZnB1     | 54      | 48.2  | 37.2  | 14.6 | 2.6ZnO.2.3B₂O₃.3.6H₂O       |
| ZnB2     | 59      | 45.1  | 42.6  | 12.3 | 2.4ZnO.2.7B₂O₃.3.6H₂O       |
| ZnB3     | 98      | 37.3  | 48.1  | 14.6 | 2ZnO.3B₂O₃.3.5H₂O           |
| ZnB4     | 91      | 39.3  | 47.2  | 13.5 | 2.1ZnO.2.9B₂O₃.3.3H₂O       |
| ZnB5     | 94      | 38.4  | 47.9  | 13.7 | 2ZnO.3B₂O₃.3.6H₂O           |
| ZnB6     | 87      | 37.6  | 49.2  | 13.2 | 2ZnO.3.1B₂O₃.3.3H₂O         |
| ZnB7     | 91      | 36.9  | 48.6  | 14.5 | 2ZnO.3B₂O₃.3.8H₂O           |
| ZnB8     | 92      | 37.2  | 48.4  | 14.4 | 2ZnO.3B₂O₃.3.5H₂O           |
| ZnB9     | 93      | 37.3  | 47.8  | 14.4 | 2ZnO.3B₂O₃.3.5H₂O           |
From the results in table 2, the sample ZnB3 will be carefully characterized by several characterization techniques.

**Crystalline and morphological characterization of nanoflower-like zinc borate nanoparticles**

The XRD pattern in figure 1 indicates the crystallinity of the obtained zinc borate ZnB3. Besides, the XRD pattern of the precursor ZnO nanoparticles was also recorded to compare the conversion of zinc oxide into zinc borate. The results reveal that the diffraction peaks observed are monoclinic 2ZnO·3B₂O₃·3.5H₂O, which is in good agreement with JCPDS file No. 09–0088. Furthermore, this result is reasonably agreed with the result of the elemental analysis in table 2. No XRD pattern peaks of ZnO precursor or H₃BO₃ were observed; thus, it demonstrates the high purity of the obtained zinc borate after the reaction.

The morphology of the obtained zinc borate ZnB3 sample and the precursor zinc oxide nanoparticles are shown in figure 2. The precursor, zinc oxide nanoparticles, presents the nanoflower-like morphology and consists of interconnected nanopetals with 20–50 nm of thickness. It is also apparent that zinc borate exhibits the nanoflower-like morphology, which is like the morphology of the zinc oxide precursor. The interconnected nanopetals of zinc borate were formed from the nanoparticles of zinc borate with a size smaller than 20 nm.

The morphology of the obtained zinc borate ZnB3 can be seen by both low-resolution and high-resolution TEM images (figure 3). The low-resolution image of TEM shows that zinc borate consists of an assembly of nanoparticles of zinc borate with the nanopetal morphology (figure 3(a)). The particle size of the zinc borate can be seen in the high-resolution image of TEM (figure 3(b)). The results show that the nanopetal of zinc borate consists of several nanoparticles with a size of about 5 nm. Thus, it may be helpful for the incorporation of zinc borate into another polymer matrix.

**FT-IR and Raman spectral characterization of nanoflower-like zinc borate nanoparticles**

FT-IR spectra of the nanoflower-like zinc borate ZnB3 and zinc oxide have been identified in figure 4. The stretching vibration of O–H groups and crystalline water appear in the FT-IR spectra of both zinc oxide and zinc borate samples. The band at 3350 cm⁻¹ indicates the stretching vibrations of O–H groups as the study [2]. Moreover, from both spectra, the stretching vibrations of the H-O-H bands can be seen between 1500–1800 cm⁻¹, which are assigned to the crystalline water incorporated in the compound [8]. Moreover, the peak at approximately 457 cm⁻¹ is related to the symmetric stretching of Zn-O, which can be seen in both spectra [22]. It is also can be seen that the bands at 1643 cm⁻¹ and 1726 cm⁻¹ indicate the stretching vibration of C=≡C and C=O functionalities, respectively [23].

Additionally, the FT-IR spectra of zinc borate show the number of bands that demonstrate various stretching vibrations of borate bands. It can be seen that the band at 1415 cm⁻¹ corresponds to the asymmetric stretching of ν₅(B₃O₃) groups [24]. The bands between 1350–1500 cm⁻¹ might be the in-plane bending of B-O-H. The bands from 1190 cm⁻¹ to 1120 cm⁻¹ correspond to the stretching vibration of the boronoxo-hydrogen [δ(B-O-H)] [25]. The bands between 860 cm⁻¹ and 800 cm⁻¹ correspond to the asymmetric stretching vibration of the four-coordinate boron to oxygen bands [ν₆(B₄O₃)] [26].

The lattice vibration of the material can be provided by Raman spectroscopy. Figure 5 shows the Raman spectrum of zinc borate ZnB3 and the precursor zinc oxide nanoparticles, respectively. In the Raman spectra of
both samples, the lattice vibration of ZnO appears at 440 cm$^{-1}$. The small peak at 340 cm$^{-1}$ also corresponds to the lattice vibration of ZnO [27].

Furthermore, the Raman spectra of zinc borate ZnB3 also displays several stretching vibrations of borate bonds. The band of $\nu_{as}(B_4-O)$ appears at 1048 cm$^{-1}$, meanwhile the band of $\nu p(B(OH)_{4})$ is observed at approximately 755 cm$^{-1}$. Moreover, the peak at 664 cm$^{-1}$ is assigned to the bending of $\gamma(B_3-O)$, the peak of $\delta$ ($B_4$–O) appears at around 578 cm$^{-1}$, and the peak at 297 cm$^{-1}$ corresponds to the bending of B$_3$-O [26].

**Thermal characterization of nano-flower-like zinc borate nanoparticles**

The thermal property of the zinc borate ZnB3 was analyzed by thermal gravimetric analysis from room temperature to 1200 °C (figures 6(a) and (b)). Figure 6(b) is the high resolution of figure 6(a). It can be seen that 2.7% of weight loss in the region 25 °C to 100 °C corresponds to the desorption of the adsorbed humidity.
Consequently, 12.3\% of weight loss from 100 °C to 270 °C is due to the loss of the crystal water in the zinc borate sample. The results fully agree with the XRD pattern result and elemental chemical results, which show 15\% of the mass weight of water (2ZnO·3B₂O₃·3·5H₂O). In addition, from figure 6(a), it is clear that the zinc borate sample is very stable at high temperatures. This demonstrates the outstanding thermal property of the synthesized sample, which is the best candidate for the fire-resistant coating application.

Conclusions

In this work, the nano-flower-like zinc borate compound was obtained by precipitation using zinc oxide nanoparticles as a precursor. To our best knowledge, the nano-flower-like zinc borate was one-step synthesized at room temperature for the first time. The XRD pattern results reveal that the nanoflower-like zinc borates are monoclinic 2ZnO·3B₂O₃·3·5H₂O. The particle size of the achieved materials is approximately 5 nm using TEM analysis. The TGA shows that the achieved zinc borate is outstanding stable at high temperatures. The result of
this work provides a new route for the fabrication of zinc borate nanoparticle, which could be widely used in many applications.

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Figure 6. Thermal gravimetric analysis of the nano-flower like zinc borate.
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