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Preparation and Characterization of Nanofibres of $2ZnO{\cdot}3B_2O_3{\cdot}5H_2O$ Ceramic Composite Using Sol-Gel Processing

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$2ZnO{\cdot}3B_2O_3{\cdot}nH_2O$ (zinc borate) having the industrially important composite and used as flame retardant, anti-smoke and semiconductor in the electronic circuits was examined with different crystal structures. In this study, nanofibers of PVA/zinc nitrate/boric acid composite were prepared by using sol-gel processing and electrospinning technique. By high temperature calcinations of the above precursor fibers, nanofibers of $2ZnO{\cdot}3B_2O_3{\cdot}5H_2O$ composite with diameters of 110 nm could be successfully obtained. The products have been characterized by X-ray powder diffraction, thermogravimetry and differential thermal analysis, scanning electron microscopy and Fourier transform-infrared spectroscopy. The effects of experimental conditions on the products were investigated.

Keywords: Nanofibers, Zinc borate composite, Sol-gel processing, Electrospinning.

INTRODUCTION

In recent years, nanostructural materials such as nanorods, nanowires or nanofibers have been studied due to both of their scientific interests and potential applications in nano devices. In particular, the dispersion of metal nanoparticles in an inorganic matrix has aroused great interest. Variety of methods suggested for the preparation of such materials, including deposition methods, ball milling technique, self-assembled mono layers and sol-gel process[1,2].

The production of zinc borate from boric acid and zinc oxide was studied using different approaches[3,4]. Those studies were mainly interested in synthesis of micron sized product and optimization of reaction parameters. However, recent studies have focused on the production of nano sized zinc borate species, as particle size of product became important in many industrial applications. The major challenge in synthesis of inorganic nanoparticles is the accurate control of particle size and morphology which is directly related to processing methods.

Recently, the sol-gel method has been combined with the electrospinning technique to produce ultrafine polymer/ceramic nanofibers. Electrospinning is a simple and inexpensive method for generating ultrafine fibers of various types of materials including polymer, polymer/ceramic composites and ceramic fibers. The electrospun nanofibers are able to form a highly porous mesh and their large surface-to-volume ratio improves performance for many applications. In the past, electrospinning has been mainly applied to polymer fibers. Recently, various micro- and nano-ceramic fibers have been obtained by high-temperature calcinations of organic-inorganic composite fibers assembled by electrospinning[5,6]. This method appears to be the most straightforward way to prepare nanofibres *via* transferring a polymer melt or solution through a spinneret using a high-voltage electrostatic field[7].

EXPERIMENTAL

Nanofiber production was carried out in three stages. The first step is the preparation of electrospinning solution using sol gel method, the second step the creation nanofibers by the method of electrospinning and finally nanofiber production by thermal treatment. In experiments, in first stage, three different (A, B and C) solutions were prepared. In second stage, to prepare for electrospinning solution, B and C solutions added to A. Combinations of these solutions are given in Table-1. The electrospinning solution obtained was filled to syringe and was placed into syringe pump. A positive electrode to the tip of the syringe, a negative electrode to collector is connected and set up the potential difference between the tip of the syringe tip and collector.

TABLE-1
COMPOSITION USED SOLUTIONS IN THE SOL-GEL PROCESSING

Solution A	$PVA/H_2O/CH_3CH_2OH$	1:10:2 (w/w/w)
Solution B	$Zn(NO_3)_2{\cdot}6H_2O/H_2O/CH_3CH_2OH/HCl$	1:10:2:1 (w/w)
Solution C	H_3BO_3/H_2O	1:10 (w/w)

RESULTS AND DISCUSSION

Scanning electron microscopy (SEM): SEM photographs of PVA/zinc nitrate/boric acid composite bers 15 kV and 10% PVA solutions was shown in Fig. 1a-b. As shown in Fig. 1a, the PVA/zinc nitrate/boric acid composite nanobers demonstrated a uniform morphology. After calcination at 500 °C (Fig. 1b), the diameters of the fibers became smaller. The diameter of nanofibers before and after calcination was determined as 818 and 110 nm, respectively. It was thought to be due to the complete removal of organic molecules and the development of zinc borate composite fibers[8].

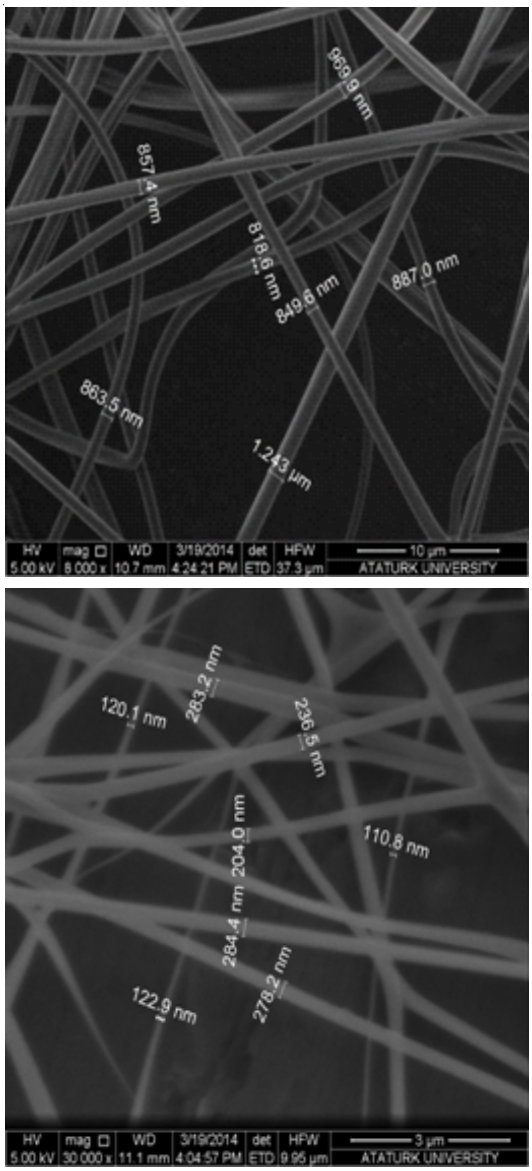

Fig. 1. (a) PVA/zinc nitrate/boric acid composite nanofibers (b) After calcination at 500 °C

FT-IR spectra: Fig. 2 displays the FT-IR spectra of the nanofibers of pure PVA, PVA/zinc nitrate/boric acid composite and the fiber composites calcined at 500 °C. As is observed in Fig. 2a, due to pure PVA, the peaks is shown, especially –OH group between 3500-3100 cm^{-1} and asymmetric and symmetric stretching band of CH_2 at around 2954 and 2095 cm^{-1}, stretching band of C-H at 2840-1455 cm^{-1}, C=O at 1714-1570 cm^{-1}, C-H at 1147 cm^{-1}, 1094 and 851 cm^{-1}, respectively stretching band of C-C and C-O[9].

As observed in Fig. 2(b-c), the vibration mode of ZnO-B_2O_3 at 3227 cm^{-1} [10], the presence of metal oxide between 600-400 cm^{-1} is due to metal oxide in 457 with 510 cm^{-1}, respectively asymmetric or symmetric stretching of BO_3 and in 1442-1356 cm^{-1} and BO_4 in 1103-1024 cm^{-1} [11], stretching band of B-O-H in 1194 cm^{-1}.

When calcinations were at 500 °C (Fig. 2c), all the peaks corresponding to the organic groups of PVA and asymmetric or symmetric stretching of CH_2 in 2954-2095 cm^{-1} disappeared and new peak at 3050 cm^{-1} was assigned to ZnO-B_2O_3 bond. For this is seen as the dominant band in the spectrum of BO_3 and ZnO-B_2O_3.

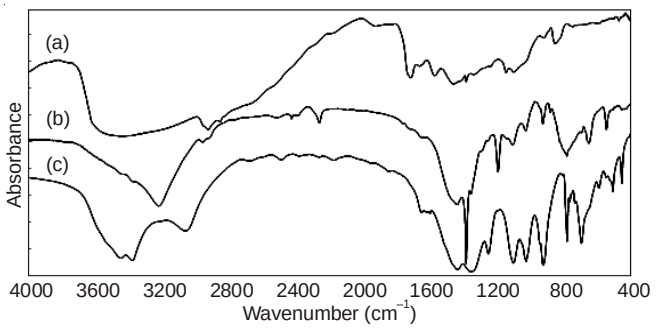

Fig. 2. (a) Pure PVA (b) PVA/zinc nitrate/boric acid composite (c) after calcined at 500 °C

TG-DTA: The results of simultaneous TG and DTA analyses of the nanofibers of PVA/zinc nitrate/boric acid composite are shown in Fig. 3. The DTA curve depicted as a endothermic peak at 129 °C, which could be attributed to the loss of moisture and trapped solvent (water, ethanol from TEOS)[12]. The endothermic peak around 389 °C could be attributed the degradation of PVA by dehydration on the polymer side chain, which was manifested by a weight loss in the TG curve at the corresponding temperature range. The other degradation between 380 and 400 °C corresponds to the decomposition of the PVA main chain which was shown in TG curve. Finally, as shown in further weight loss the endotherm

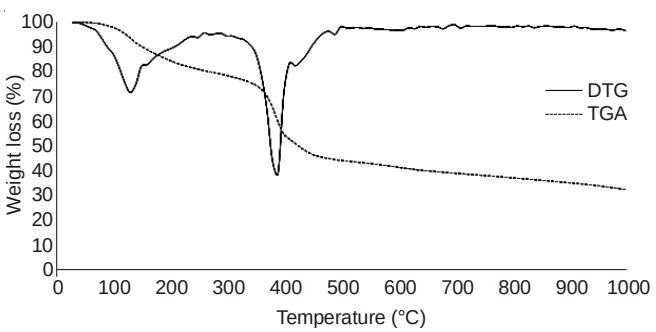

Fig. 3. TGA-DTA curves of PVA/zinc nitrate/boric acid composite

at around 458 °C in DTA curve, inorganic component, between 500 °C and 1000 °C indicated the formation of pure inorganic oxide in a crystalline form.

X-ray diffraction (XRD): The analysis of the crystal structure of the calcined samples at 500 °C was conducted by XRD (Fig. 4). When analysis of peaks, in terms of 2θ, the boric peaks acid are observed at 14.4°, 27.8°, 30.3°, 31.3°, 40.2°, 41.5°, 42.9° and 44.3° (JCPDS 30–0199) and the zinc oxide peaks are observed at 31.6°, 34.3°, 36.1°, 47.4°, 56.5°, 62.7°, 66.3°, 67.8° and 69.0° (JCPDS 80–0075). The XRD patterns of synthesized zinc borate are consistent with that of 5 mol hydrated commercial zinc borate ($2ZnO{\cdot}3B_2O_3{\cdot}5H_2O$)[13]. In this case, it is understood that zinc borate was synthesized.

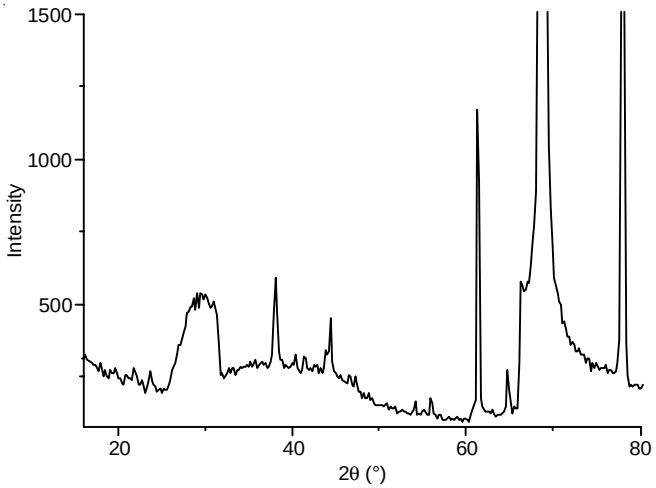

Fig. 4. XRD patterns of the PVA/zinc nitrate/boric acid composite nanofibers calcined at 500 °C

From the well-known Scherrer formula the crystallite size, D, is:

$$D = \frac{K{\cdot}\lambda}{B{\cdot}\cos\theta}$$

where λ is the X-ray wavelength (0.15405 nm), B is the peak value of the full width at half maximum (FWHM) in radians and K is the shape factor and takes values between 0.8-1 according to the shape of the crystal. θ is half of the angle of Bragg reflection. The value of β in 2θ axis of diffraction profile must be in radians. According to the Scherrer equation, the crystal sizes of the synthesized zinc borate are between 39 nm and 50 nm.

Conclusion

In conclusion, nanofibers of PVA/zinc nitrate/boric acid composite have been successfully prepared by using sol-gel processing and electrospinning technique and then by calcination at 500 °C of the obtained nanofibers with this way, before calcination $2ZnO{\cdot}3B_2O_3{\cdot}5H_2O$ nanofiber with diameters of average 818 nm was obtained. After calcination nanofiber with diameters of average 110 nm was obtained. This value is very important for uses place of nanofiber. The obtained $2ZnO{\cdot}3B_2O_3{\cdot}5H_2O$ composite nanofiber could be suggesting for catalysis application. This route is simple and effective to produce nanofibers of mixed inorganic oxide composite.

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