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Fibrous zinc oxide prepared by combined electrospinning and solvothermal techniques

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Abstract

The synthesis of novel zinc oxide (ZnO) nanostructure consisting of ZnO nanoparticles formed into the network of fibers was investigated. This structure was fabricated from the solvothermal reaction of the poly(vinyl alcohol) (PVA)/zinc acetate composite fibers, which were firstly prepared by electrospinning technique. It was found that zinc acetate within the PVA matrix was converted into ZnO nanoparticles in hexagonal wurtzite structure, while PVA was still retained within the structure. Therefore, the product was no longer easy to crumble into powder, easy to handle, yet it still possessed nanostructure feature. The growth mechanism of ZnO nanoclusters within the structure was also proposed by investigating the effects of various parameters, i.e. content of zinc acetate within the fibers, reaction temperature and reaction time.

Keywords: D. ZnO; Nanostructures; Electrospinning; Solvothermal

1. Introduction

Zinc oxide (ZnO) is a polar inorganic crystalline material with a wide direct band gap. It has received considerable attention because of its unique optical, semiconducting, piezoelectric and magnetic properties. ZnO is also considered as an effective, inexpensive, nontoxic catalyst, suitable for various photocatalytic reactions. In some cases, the photocatalytic activity of ZnO is reported to be higher than that of titanium (IV) oxide (TiO_2) [1].

For the application in photocatalysis, large surface area of ZnO structure is preferred. As a result, the use of nanosized ZnO as a photocatalyst has recently gained a lot of attention. One technique to synthesize nanosized powder is the solvothermal method. It is a wet chemical route, in which an organic solvent acts as a reaction medium that allows crystallization of inorganic substances to be achieved at a relatively low temperature [2]. The solvothermal synthesis is one of the most powerful tools for providing distinct morphologies of nanoparticles [3]. ZnO nanoparticles with high crystallinity have also been prepared successfully, in one step, by this method [3,4]. Nevertheless, direct use of the nanosized powder with a fluid reactant, e.g. liquid or gas, is often limited by handling problems, such as the loss of the powder with the fluid stream and the problem with the post-operational recovery of the powder. The conventional means for solving such problems is the processing of the fine powder into porous granules, which are much easier to handle. However, granulation often results in a significant decrease in photocatalytic activity because only the outer surface of the granules is exposed to the radiation.

In the present study, a novel nanostructure in the form of nanofibers consisting of nanosized ZnO grains is presented. This structure still possesses large exposed area of the nanoparticles, yet it is easy to handle owing to the extremely high aspect ratios of the products which could reach millimeters in length. This nanostructure was fabricated by the combined techniques of solvothermal and electrospinning.

Electrospinning is a facile technique for fabricating materials of diverse origins into fibers with diameters approaching the nanometer length scale. This technique relies on the electrostatic charging of a liquid droplet and the subsequent ejection of the liquid in form of a jet by means of associated electrical forces [5]. Electrospinning has also been

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used to synthesize inorganic fibers by firstly spinning a polymer solution containing an inorganic precursor into composite fibers. The inorganic precursor inside the as-spun fibers is then converted into inorganic oxide by means of calcination at high temperature, which simultaneously removes the polymer matrix [6]. However, the resulting products are often brittle and easily crumbled into fine powder. To refrain that from happening, we intended to retain the polymer within the fibers such that the integrity of the nanostructure was retained. The inorganic precursor was converted into its oxide via the solvothermal process, instead of the conventional calcination. The present study was conducted primarily to investigate the morphology of the products as well as the mechanisms governing the synthesis and the crystal growth.

2. Experimental

2.1. Fabrication of precursor nanofibers via electrospinning technique

Poly(vinyl alcohol) (PVA) with a weight-average molecular weight of 72,000 Da (Fluka, USA) and zinc acetate (99.99%, Aldrich, USA) were used as the starting materials for preparing the precursor fibers. An aqueous solution of PVA was first prepared by dissolving PVA powder in warm deionized water. Then, zinc acetate was slowly added to the PVA solution and the mixture was stirred vigorously for 3 h. The mixture was kept at room temperature for 8 h, during which zinc acetate within the mixture underwent sol–gel transformation. A viscous gel of PVA/zinc acetate obtained at the end of the process was referred to as the spinning solution. The concentration of PVA in the solution was 8 wt.%, while the mass ratio between zinc acetate and PVA was varied from 1:3, 2:3 and 1:1, respectively.

Each of the spinning solutions was immediately loaded into a plastic syringe equipped with a blunt-ended 20-gauge stainless steel needle. The emitting (positive) electrode from a Gamma High Voltage Research ES30PN power supply capable of generating DC voltages up to 30 kV was attached to the needle. The grounding electrode from the same power supply was attached to a piece of aluminum foil, which was used as the collector plate, placed approximately 15 cm below the tip of the needle. Upon the application of the electrical potential of 19 kV across the needle and the collective plate, a fluid jet was ejected from the nozzle. As the jet accelerated towards the collector, the solvent evaporated, leaving only ultrathin fibers as a non-woven mat on the collector. The obtained fibers were left exposed to the ambient atmosphere for approximately 1 day.

2.2. Conversion of precursor fibers into ZnO nanostructure by solvothermal technique

PVA/zinc acetate composite fibers were used as starting materials in the solvothermal process. They were suspended in 100 mL of 1-octanol, used as solvent, in a test tube. The test tube was then placed in a 300-mL autoclave. In the gap between the test tube and the autoclave wall, 30 mL of the same solvent was added. After the autoclave had been completely purged with nitrogen, the autoclave was heated to a desired temperature ranging from 170 to 250 °C at a rate of 2.5 °C/min and held at that temperature for 0–2 h. It should be noted that 0 h of the holding time represented the system that was cooled down immediately after it had reached the desired temperature. The pressure inside the autoclave reactor increased autogenously and gradually as the temperature increased and the reaction proceeded. After the holding period, the autoclave was cooled to room temperature. The resulting products were collected after repeatedly washed with methanol and characterized by X-ray diffraction (XRD, SIEMENS D5000), scanning electron microscopy (SEM, JEOL JSM5800), infrared spectroscopy (FT-IR, NICOLET IMPACT400) and thermogravimetric analysis (TGA, PERKIN-ELMER PYRIS DIAMOND).

3. Results and discussion

3.1. Properties of as-spun precursor fibers

The precursor fibers, i.e., PVA/zinc acetate composite fibers, as obtained from the electrospinning technique are smooth without the presence of beads (see Fig. 1). No ZnO was detected in the fibers (XRD analysis result not shown). Diameters of these fibers were in the range of about 100–500 nm, depending on the content of zinc acetate originally loaded in the spinning solution. The greater the concentration of zinc acetate in the spinning solution was, the larger the fibers would be. It should be noted that, as the concentration of zinc acetate is increased, not only that the diameter of the as-spun fibers is increased, but also the distribution becomes broader as well (see Fig. 2). This is a result of the increase in the viscosity of the spinning solution because of the gelation of zinc acetate within the spinning solution. The increased viscosity can lead to non-uniform ejection of the jet [7,8] and it is hence responsible for the broad diametric distribution of the fibers prepared from the spinning solution containing high content of zinc acetate.

3.2. Formation of ZnO nanostructure by solvothermal reaction of the precursor fibers

Regardless of the content of zinc acetate in the precursor fibers, all resulting products from the solvothermal process at 250 °C were found by XRD analysis to be ZnO in its wurtzite structure without the contamination from other crystalline phases. However, TGA analysis revealed two steps in the loss of the mass at temperatures up to 500 °C, beyond which there was no change in the mass of the sample. The thermal behavior is similar to that of the pristine PVA fibers, although the loss in the mass of the pristine PVA fibers occurs in a much greater extent. These results suggest that zinc acetate within the precursor fibers was converted, either in whole or in part, into ZnO, while PVA still remained within the fibers.

Preliminary investigation of the products from the solvothermal process revealed that they still had elastic properties of PVA. The final products are bendable with no sign of cracking and therefore are no longer easy to crumble

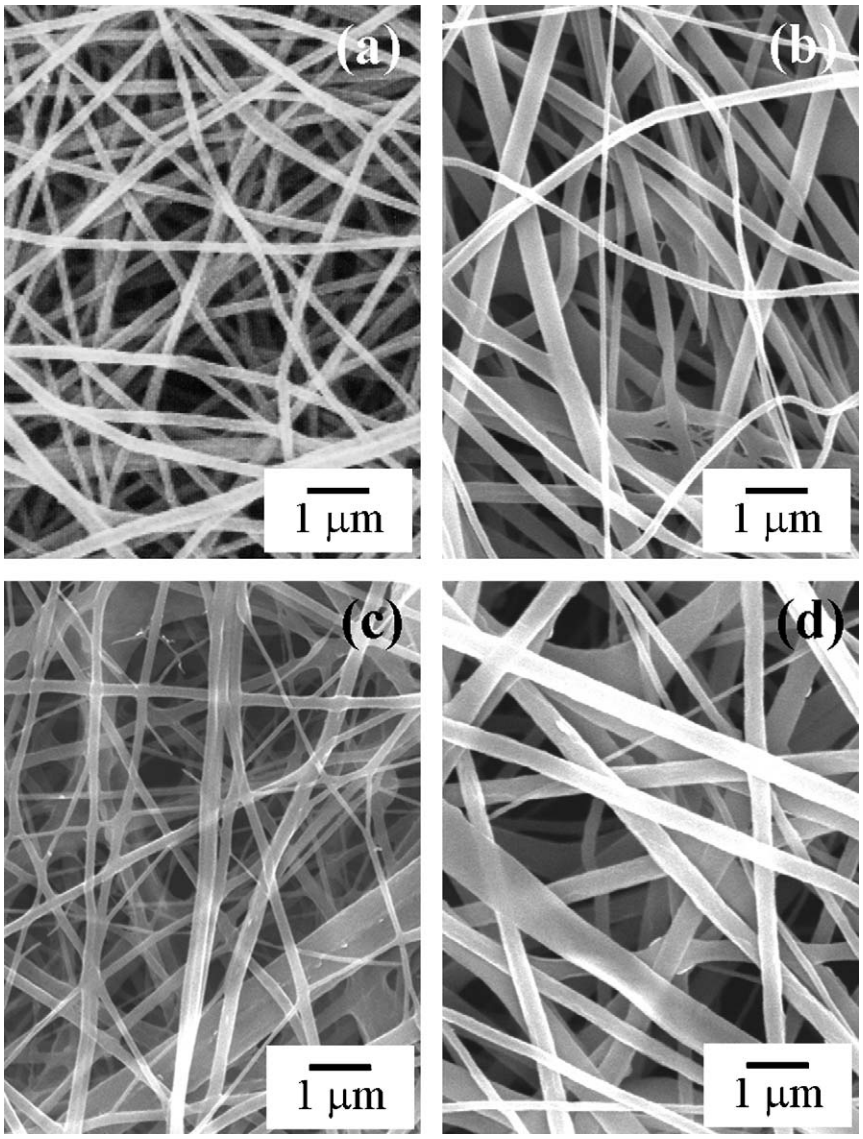

Fig. 1. Representative SEM micrographs of as-spun precursor fibers prepared from the spinning solutions in various zinc acetate-to-PVA ratios: (a) pristine PVA, (b) 1:3, (c) 2:3 and (d) 1:1.

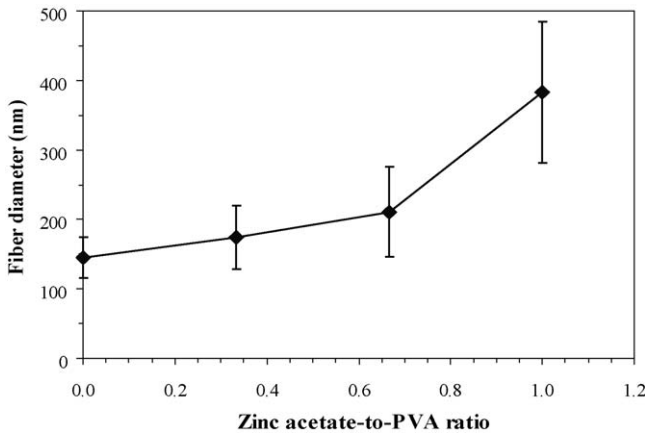

Fig. 2. Diameters of as-spun precursor fibers as a function of zinc acetate content. The error bars in the figure represent standard deviation of the fiber diameter data.

into powder. Fig. 3 compares FT-IR spectra of the precursor fibers and the final product. The major characteristic absorption bands of PVA, i.e., at 2925 cm^{-1} (CH and CH_2 asymmetric stretching), 1440 cm^{-1} (CH_2 bending), 1336 cm^{-1} (O–H bending and C–H wagging), 1092 cm^{-1} (C–O stretching) and 858 cm^{-1} (CH_2 rocking) [9], and those of zinc acetate, i.e., at 1577 cm^{-1} (C=O stretching) and 1425 cm^{-1} (C–O stretching) [10], are discernible from the precursor fibers. All of the observed absorption bands agree well with the values reported in literatures for the pristine compounds, which suggests that zinc acetate was dispersed in the precursor fibers without any chemical interaction with PVA. The solvothermal products also show similar FT-IR spectra of PVA as that of the precursor fibers, but the intensities of the absorption bands are significantly reduced. This indicates that although part of PVA is removed from the precursor fibers during the solvothermal reaction, PVA still remains in the final products.

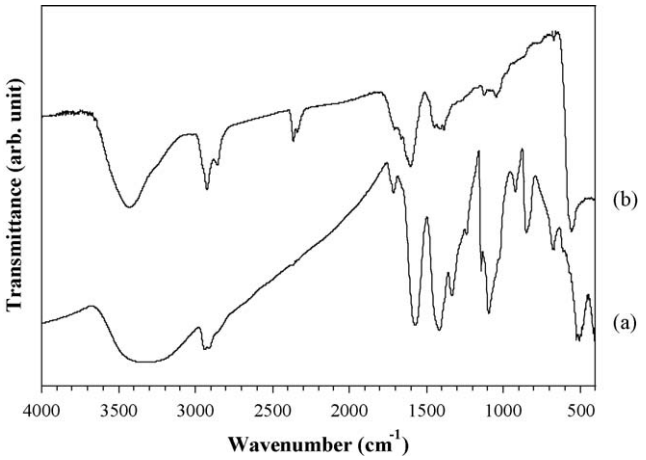

Fig. 3. FT-IR spectra of: (a) precursor fibers and, (b) ZnO product from the solvothermal process at 250 °C for 2 h.

Small fraction of the unreacted zinc acetate remaining in the products after the solvothermal process at 250 °C for 2 h is also observed. However, it should be noted that the absorption bands of zinc acetate shift from 1577 and 1425 cm^{-1} to 1600 and 1441 cm^{-1}, which indicates that the structure of zinc acetate changes from the unidentate type into the bridging complex during the solvothermal reaction [10]. The reaction finally yields ZnO as witnessed from a strong absorption band of Zn–O stretching around 430–550 cm^{-1} [11]. The results from FT-IR analysis confirm the XRD and the TGA results that the final product contains both the remnant amount of PVA and the newly generated ZnO. The overall specific surface area of the products is in the range of 9–16 m^2/g, which is slightly higher than that of ZnO nanoparticles synthesized by the conventional solvothermal technique [12].

3.3. Effects of zinc acetate content

Fig. 4 shows representative SEM images of ZnO products synthesized by the solvothermal reaction at 250 °C for 2 h, using the precursor fibers containing various zinc acetate contents as the starting materials. While no remnant of the fiber form is observed for the solvothermal product of the pristine PVA fibers, the underlying fibrous structure of the solvothermal products of the precursor fibers is still discernible. Evidently, the surfaces of these fibers are rough. The results suggest that the dispersed zinc acetate clusters in the PVA matrix of the precursor fibers could act as nucleation sites upon their conversion to ZnO. As the formation of ZnO is initiated by the esterification reaction between zinc acetate and 1-octanol [4], further growth of ZnO crystals is localized and limited within the PVA matrix. At the junction of fibers, however, the growth of ZnO nanocrystals on the fibers could also results in the coalescence of the products into larger entities. As previously mentioned, the pristine PVA fibers lose the fibrous structure after they had been subjected to the solvothermal process, due likely to the dissolution of PVA in 1-octanol at the treatment temperature. It is therefore suggested that zinc acetate within the precursor fibers had to be converted into ZnO prior to the dissolution of PVA in 1-octanol which would have caused the precursor fibers to lose their fibrous structure.

Diameters of the obtained ZnO fibers are increased with an increase in the zinc acetate content in the precursor fibers (see Fig. 5), mainly because of the observed increase in the size of the as-spun precursor fibers with the zinc acetate content. However, the crystallite size of ZnO, as calculated from the line broadening of the XRD pattern, is also increased with zinc acetate content. This result indicates the increase in crystal growth with the amount of zinc acetate dispersed in the precursor fibers. It should also be noted that the average size of ZnO particles on the fibers, as observed from the SEM images, is almost one order of magnitude larger than the crystallite size calculated. Therefore, all ZnO nanoparticles embedded within the products are polycrystalline in nature.

3.4. Effects of reaction temperature and reaction time

The formation of ZnO nanoparticles within the PVA fiber matrix was further investigated by now paying attention to the effects of the solvothermal reaction temperature and time. The results from the XRD analysis of the obtained products from the solvothermal process under various conditions show that all samples are ZnO in its wurtzite structure as shown in Fig. 6. Nevertheless, if the reaction temperature is lower than 250 °C, the XRD analysis reveals peaks at the diffracted angles (2θ) of around 22.5° and 41°, which are main peaks of zinc acetate [4], as well as a peak at 2θ of around 20°, corresponding to the (1 0 1) planes of the semi-crystalline PVA [13], in addition to those for ZnO. The intensity of the peaks associated with zinc acetate decreases with an increase in either the reaction temperature or the reaction period, which accommodates the decomposition of zinc acetate into ZnO. A similar trend was observed for the PVA component as well. For PVA, however, it is indicated that the crystallinity of PVA is decreased since PVA can dissolve into 1-octanol in greater extent at higher temperature. It should also be noted that only a trace amount of ZnO was obtained when the reaction temperature was lower than 170 °C.

Fig. 7 shows representative SEM images of the ZnO nanostructures that had been synthesized at various reaction conditions. All of the obtained products are still in the fiber form, although their shape is somewhat distorted. For the products synthesized at 170 °C, the average fiber diameter and the size of the ZnO particles on the fibers increase when the reaction period is prolonged. This relates to the fact that zinc acetate is not completely decomposed into ZnO at such a low temperature as already witnessed from the XRD analysis, while PVA still remains within the fibers. At this temperature, PVA may be swollen or the partially decomposed zinc acetate within the fibers may aggregate into clusters as the solvothermal reaction proceeds. For the products synthesized at 200 °C, it can be seen that the fibers become thinner during the heating-up from 170 to 200 °C (comparing between Fig. 7a and b). This is the result from the fact that substantial fraction of zinc acetate is converted into ZnO at this temperature [4]. However, if the reaction is held at 200 °C for 2 h, the average size of the ZnO

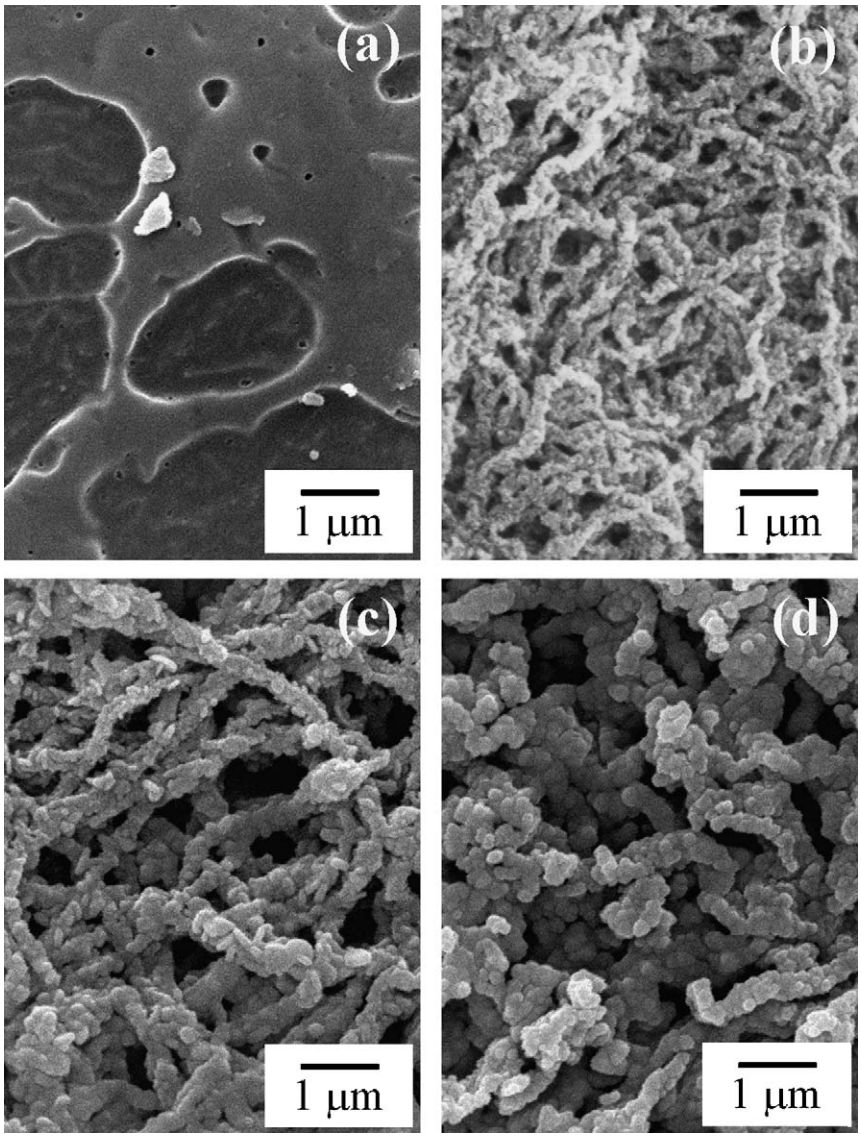

Fig. 4. Representative SEM micrographs of ZnO products prepared from the solvothermal process at 250 °C for 2 h, using the precursor fibers with various zinc acetate-to-PVA ratio: (a) pristine PVA, (b) 1:3, (c) 2:3 and (d) 1:1.

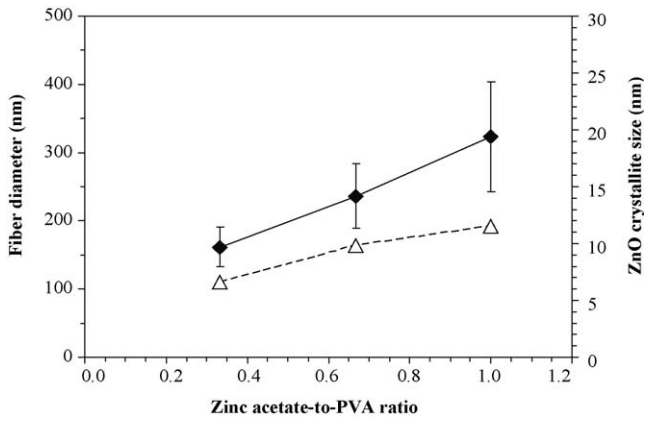

Fig. 5. Diameter (—) and crystallite size (- - -) of ZnO solvothermal products as a function of zinc acetate content. The error bars in the figure represent standard deviation of the fiber diameter data.

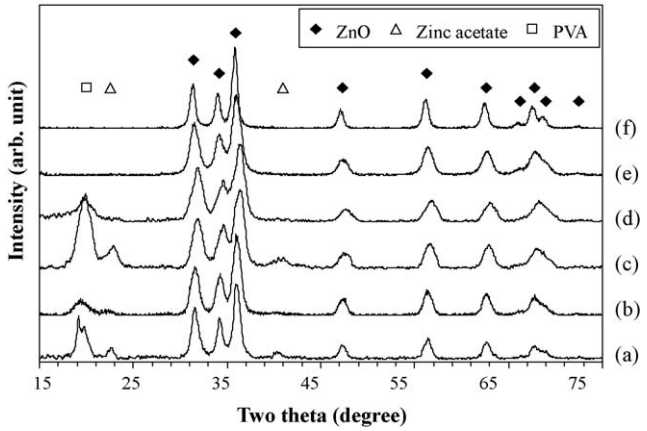

Fig. 6. XRD patterns of ZnO products prepared from the solvothermal process at various conditions: (a) 170 °C for 0 h, (b) 170 °C for 2 h, (c) 200 °C for 0 h, (d) 200 °C for 2 h, (e) 250 °C for 0 h and (f) 250 °C for 2 h.

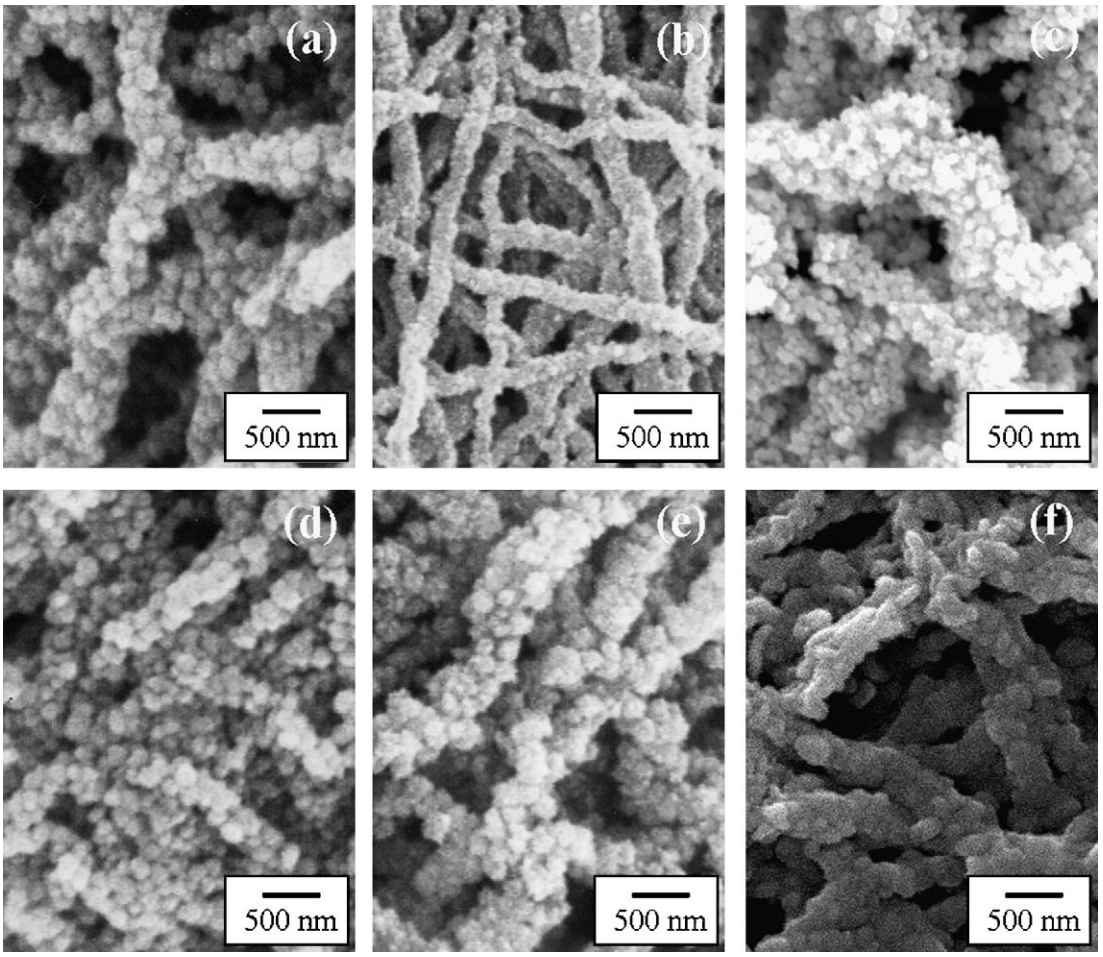

Fig. 7. Representative SEM micrographs of ZnO products prepared from the solvothermal process at various conditions: (a) 170 °C for 0 h, (b) 200 °C for 0 h, (c) 250 °C for 0 h, (d) 170 °C for 2 h, (e) 200 °C for 2 h and (f) 250 °C for 2 h.

particles within the fibers increases due to the growth of the ZnO crystallites. Finally, for the reaction at 250 °C, it is evident that the growth of ZnO nanoparticles has occurred during the heating-up process from 200 to 250 °C. On the other hand, when the system is held at 250 °C for 2 h, the fiber diameters decrease because greater proportion of the PVA matrix within the fibers dissolves into the surrounding solvent at this temperature. At temperature higher than 250 °C, however, the product loses its fibrous structure and only ZnO nanoparticles were found as suspension in the autoclave.

4. Conclusion

ZnO nanostructure in a form of beaded fibers was successfully synthesized by combined electrospinning and solvothermal techniques. Zinc acetate within the PVA matrix of the precursor fibers undergoes decomposition via the solvothermal process and forms nucleation sites for the growth of ZnO nanoparticles on the fibers. Size of the ZnO particles as well as diameter of the product depends upon the concentration of zinc acetate within the precursor fibers. The grain growth is enhanced by the solvothermal reaction temperature, yet it proceeds as the solvothermal reaction is prolonged.

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