Fabrication and characterization of zinc oxide nanofibers for renewable energy applications

Muhammad Imran, Sajjad Haider, Kaleem Ahmad, Asif Mahmood, Waheed A. Al-masry

Department of Chemical Engineering, College of Engineering, King Saud University, P.O. Box 800, Riyadh 11421, Saudi Arabia
Sustainable Energy Technologies Center, King Saud University, Riyadh, Saudi Arabia

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Abstract Nanometer (nm) scale 1D zinc oxide (ZnO) nanofibers were fabricated through sol–gel processing and electrospinning of Polyvinyl alcohol (PVA) and zinc acetate precursors. The structure and morphologies of the zinc acetate/PVA precursor and ZnO nanofibers were studied by Fourier transform infrared (FTIR), X-ray diffraction (XRD), thermogravimetric analysis (TGA) and field emission scanning electron microscopy (FE-SEM). Bead free smooth nanofibers with increased average diameters (278 nm (5 wt.%) and 423 nm (15 wt.%)) were obtained as the content of zinc acetate precursor was increased. The calcination temperature of 480 °C was determined from TGA. FTIR, XRD and TGA studies carried out after calcinations, confirmed the formation of ZnO nanofibers by the appearance of a band at 472 cm⁻¹, characteristic ZnO pattern (i.e. peaks at 24.3182, 34.331, 36.496, 47.569 and 57.168 2θ degrees) and no weight loss after 480 °C, respectively. The burning of polymer has also been confirmed by a significant decrease in average diameter (124 nm (5 wt.%) and 197 nm (15 wt.%)) of the ZnO nanofibers. Electrospinning has been found to be a simple and cost effective technique for the synthesis of 1D ZnO nanofibers mats for potential applications in the renewable energy devices.

1. Introduction

The world in 21st century is facing severe energy and environmental problems originating from the consumption of conventional fossil fuel. To meet the growing energy demand for greater urbanization, huge industrialization and higher population growth the dependency on the conventional fossil fuel should be shifted to the sustainable energy resources (Li et al., 2012). With the advent of nanotechnology, a flurry of research is underway to seek new solutions for sustainable clean energy (Dai et al., 2011; Dong et al., 2011). Since there is a direct correlation between the shape, size and structure of materials, and their physical/chemical properties, it is therefore imperative to control these parameters. Nanofibers possessing fine diameter, fibrous morphology and large surface area have gained special interest of researchers to solve the several environmental and energy issues (Ramakrishna et al., 2006). For example the use of electrospun nanofibers as a metal oxide electrode in dye sensitized solar cell and fuel cell increases their energy conversion efficiency (Chuangchote et al., 2008). In addition, there is a great interest to find the simple cost effec-
tive method to prepare ID nanofibers in bulk form. Among various synthetic techniques, electrospinning is a simple and effective method for the fabrication of these nanofibers in bulk (Haider et al., 2012; Haider and Park, 2009).

Currently, zinc oxide (ZnO) nanofibers have been placed among the category of front runner nanomaterials (carbon nanotube and silicon nanowires) due to its remarkable semiconducting, piezoelectric and photo-conducting functional properties (Liu et al., 2011; Wu et al., 2011; Sangkhaprom et al., 2010). These have enormous technological applications in energy devices for example light emitting diode, optoelectronics devices, varistor, gas sensors, solar cell, etc.

Traditional dye sensitized solar cell possesses limited energy conversion efficiency due to the high interface scattering and restricted mobility caused by the recombination of electrons before reaching the electrode. The use of ZnO nanofibers as photoelectrode provides an alternative route to improve the energy conversion efficiency of the solar cell due to enhanced surface activity. In this work ZnO nanofibers were fabricated by the simple electrospinning technique. The effect of the systematic addition of zinc acetate to PVA on the morphology of resulting zinc acetate/PVA precursor and ZnO nanofibers was investigated for potential applications in renewable energy devices.

2. Experimental

2.1. Methods and materials

Medium molecular weight zinc acetate powder and PVA were purchased from Sigma–Aldrich and Alfa Aesar, respectively. All the chemicals were of analytical grade and were used without further purification. Distilled water was used for the preparation of PVA solution.

2.2. Solution preparation and electrospinning

Standard precursor solution method was used to prepare nanofibers through electrospinning. PVA and zinc acetate precursor were used as starting materials. First 1.5 g PVA was dissolved ultrasonically in 10 mL deionized water in a sonicator bath (Branson Model 2510) at 70 °C for 90 min. The solution was subsequently magnetically stirred at 70 °C for 3 h. When a homogenous transparent gel solution has been achieved it was then electrospun by optimizing the different processing parameters. The solutions were added to a 5 mL plastic syringe of 10 mm diameter with stainless steel needle of 0.8 mm diameter. The syringe was placed in syringe pump and the needle was connected with a high voltage supply, which could generate a high voltage of up to 30 kV. The conditions used to produce PVA nanofibers via electrospinning were optimized as; needle to collector distance of 15 cm, flow rate of 0.3 mL/h and voltage of 25 kV. In the next step, 5 wt.% zinc acetate/PVA (w/v) homogenous transparent gel solution was prepared. The solution was added to a plastic syringe and by using a cylindrical drum as a counter electrode; the zinc acetate/PVA nanofibers were collected. After electrospinning the nanofibers were removed from the aluminum foil (rolled on the rotating drum), dried in the vacuum oven at 120 °C and stored in the desiccator for further characterizations. Similarly, PVA/zinc acetate nanofibers for 10 wt.% and 15 wt.% were fabricated using the same processing conditions. The samples were dried in a vacuum oven and stored for characterization.

Figure 1 FESEM micrographs of the PVA electrospun nanofibers with different % of zinc acetate: (a) 0 wt.% zinc acetate, (b) 5 wt.% zinc acetate, (c) 10 wt.% zinc acetate and (d) 15 wt.% zinc acetate.
2.3. Morphology study

The morphologies of the zinc acetate/PVA precursor and ZnO nanofibers were studied by using a FE-SEM (Hitachi S-570). The samples were fixed onto a holder with aid of a carbon tape and then placed in the sputtering machine for platinum coating to increase their electrical conductivity. After platinum coating the samples were examined by FE-SEM under high vacuum.

2.4. TGA study

Thermal behavior of the PVA and zinc acetate/PVA nanofibers was studied by TGA (TA Q50). Each sample was placed in a platinum plate, weighted and heated under nitrogen atmosphere at 10 °C/min from 25 to 600 °C. The zinc acetate/PVA nanofiber sample was further calcined at 480 °C with dwell time of 4 h.

2.5. FT-IR study

Infrared spectra of the zinc acetate/PVA precursor and ZnO nanofibers were studied by using FT-IR spectrometer (Bruker Vertex 70). For the FT-IR characterization, the KBr disks of the samples were prepared by mixing and grinding the samples with KBr powder in mortar with a pestle. The mixture was then shaped into disks under hydraulic pressure. The sample disks were placed into FT-IR and spectral measurements were recorded in the wavenumber range of 500–4000 cm⁻¹. The data were processed by using Software OPUS 6.0 (Bruker), which was baseline corrected by rubber band method with CO₂ and H₂O bands excluded.

2.6. XRD study

Crystal structure determination of the zinc acetate/PVA precursor and ZnO nanofibers was achieved with a Rigaku Ultimate IV X-ray diffractometer using CuKα (1.5406 Å) radiation at room temperature.

3. Results and discussion

3.1. Morphology of precursor nanofibers

Fig. 1 shows the morphology of the PVA nanofibers with different concentrations of zinc acetate ranging from 0 to 15 wt.%. Addition of zinc acetate did not show any effect on the morphology (beadless and smooth nanofibers were obtained (Fig. 1 b–d)), however, it did affect the average diameter of the nanofibers. The average diameter of 5 wt.% zinc acetate/PVA nanofibers was 278 nm. The addition of 10 and 15 wt.% of zinc acetate to PVA not only increased the diameter (from 345 nm (Fig. 1 c) to 423 nm (Fig. 1 d)) but also its distribution became broader. There are two factors which account for this effect. As we increase the concentration of the zinc acetate, gelation in the solution increases which leads to an increased diameter ((Fig. 2) Wu and Pan, 2006). Whereas increased viscosity leads to broader distribution of the nanofibers’ diameter (Fig. 3) due to non-uniform ejection of the jet.
The increase in the average diameter of the nanofibers with increase in the zinc acetate content is in accordance with the proposed simple linear equation (Sangkhaprom et al., 2010; Wu and Pan, 2006). The linear equation is given as follows:

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AFD = mx + D_o
\]

where "\(D_o\)" is the average fiber diameter of pristine PVA, "\(x\)" is the zinc acetate concentration in wt.\% and "\(m\)" is a constant coefficient.

3.2. TGA study

Fig. 4 shows the TGA thermograms of PVA and zinc acetate/PVA nanofibers. The thermogram for PVA showed two stages of degradation. The first weight loss occurred until 324 °C (62.33%) and the second until 595 (21.14%). For zinc acetate/PVA nanofibers four stage degradation was observed. The initial weight loss occurred until 71 °C (5.36%) and the final until 480 °C. The total weight loss between 71 and 480 °C was 68.04%. It can be inferred from the thermograms that the first loss was due to water evaporation, where as the weight loss beyond 71 °C might be due to the decomposition of organic components of zinc acetate and PVA polymer (Look, 2011). The degradation of the zinc acetate/PVA became constant beyond 480 °C. The no further loss in weight suggests the presence of only pure inorganic contents. The calcination temperature is above 480 °C and is in accordance with the other studies (Sangkhaprom et al., 2010; Wu and Pan, 2006).

3.3. Morphology of calcinated nanofibers

Fig. 5 shows the morphologies of ZnO nanofibers after calcination and with different wt.% zinc acetate. The calcined nanofibers have a smooth surface (Fig. 5a and b) and almost a uniform diameter throughout the whole length. However, some traces of residuals burnt organics are visible in the higher concentrations ZnO nanofibers (Fig 5c). The average diameter of the nanofibers decreased (from 278 to 124 (5 wt.%) and from 423 to 197 (15 wt.%) after calcination which might be due to the decomposition of organic materials. The decrease in diameter complements TGA study (Wu and Pan, 2006; Viswanathamurthi et al., 2004).
3.4. FT-IR study

Fig. 6 shows the FT-IR spectra of 15 wt.% zinc acetate/PVA precursor and calcined nanofibers at 480 °C for 6 h. In zinc acetate/PVA precursor nanofibers, the strong cyclic bands between 500 and 2000 cm\(^{-1}\) may be attributed to the stretching and bending frequencies of O–H, C'–C, C–H of PVA. All the described peaks are vanished in the calcined nanofibers. The calcined IR spectra showed a well-defined pattern of ZnO with intense peaks at 31.820, 34.331, 36.496, 47.569 and 57.168 2θ degree (Fig. 7). The appearance of the characteristic ZnO peak pattern clearly shows that PVA is decomposed and the nanofibers are composed of ZnO.

3.5. XRD study

Fig. 7 shows the XRD spectra for zinc acetate/PVA precursor and calcined nanofibers at 480 °C. XRD spectrum of zinc acetate/PVA precursor nanofibers showed no distinct peak since the material is amorphous. The small peak around 10.97 might be due to some contamination. However, zinc acetate/PVA precursor nanofibers after calcination showed a well-defined pattern of ZnO with intense peaks at 31.820, 34.331, 36.496, 47.569 and 57.168 2θ degree (Fig. 7). The appearance of the characteristic ZnO peak pattern clearly shows that PVA is decomposed and the nanofibers are composed of ZnO.

4. Conclusions

Metallic electrospun nanofibers have emerged as high-performance materials for providing solutions to obtain clean energy in the 21st century. ZnO nanofibers were fabricated successfully by the electrospinning method using zinc acetate and PVA. FTIR and XRD studies carried out after calcinations, confirmed the formation of ZnO nanofibers by the appearance of a band at 472 cm\(^{-1}\), and characteristic ZnO pattern (i.e. peaks at 31.820, 34.331, 36.496, 47.569 and 57.168 2θ degree), respectively. ZnO nanofibers possessed excellent surface morphologies and diameter in the range of 124–197 nm. The addition of zinc acetate has significantly affected the surface morphology and diameter of ZnO nanofibers. By tuning processing parameters 1D ZnO nanofibers can be fabricated with desired properties for applications in clean energy.

References


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