International Journal of Current Science, Engineering & Technology ISSN : 2581-4311
Original Research Article | Open Access | AMCT 2017 Malaysia | *Special Issue*

Effect of Calcination Temperature on Microstructural Evolution of Electrospun ZnO Fibers

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ABSTRACT. Development of portable or wearable devices demands for flexible, lightweight or even foldable materials for fabrication. In this respect, electrospinning offers a cost-effective, high throughput, versatile and scalable route for the production of flexible micro/nanofibers on almost all kinds of surfaces. In this work, semiconducting ZnO fibers of high aspect ratios were electrospun from organic precursor of ZnO solution. The effect of calcination temperature on the microstructures of the electrospun fibers was investigated. Simultaneous thermal analysis (STA) was used to monitor the temperature at which the organic precursor was removed to form ZnO. X-ray diffraction (XRD), on the other hand, was used to monitor the phase formations at various heating stages. Field emission scanning electron microscope (FESEM) equipped with energy dispersive spectrometry (EDX) was employed for morphological study of the ZnO produced. Continuous single phase ZnO fibers started to form at a temperature of around 460 °C and evolved through various stages of microstructural formations, from tubular-like structures to segmentation of granular structures and hierarchical structures at further increases in calcination temperatures. The ZnO fibers experienced increasing crystallinity and stoichiometry change during the heating process. When mechanically bent, the fibers were able to generate current pulses of between 0.1 to 10 nA.

Keywords: *Zinc oxide, Electrospinning, Calcination;*

Received: 15.10.2017, Revised: 15.12.2017, Accepted: 30.02.2018, and Online: 20.03.2018;

DOI: *10.30967/ijcrset.1.S1.2018.57-62*

Selection and/or Peer-review under responsibility of Advanced Materials Characterization Techniques (AMCT 2017), Malaysia.

1. INTRODUCTION

ZnO is an n-type semiconductor that possesses richness in growth geometries, from rod, tube to more complex morphologies such as hexagonal plate-like or flower-like structures [1-3]. Due to its unique properties such as large excitation binding energy (60 meV) at room temperature, wide band gap (3.37 eV), thermal stability, large piezoelectric coefficient and irradiation resistance, it has been used as the building blocks in various solid state devices such as sensors, cosmetics, liquid crystal displays, optoelectronics, photovoltaic and piezoelectric devices [4-6]. Moreover, ZnO has a polar crystalline structure which produces a noncentrosymmetric charge gradient in the crystal lattice when subjected to an external force. Such property has made ZnO nanofibers good candidate materials for piezo generators as these nanostructures are ultrasensitive in converting mechanical forces to high output voltages due to their high degree of flexibility for deformation [7].

ZnO fibers can be fabricated using electrospinnning, a simple, cost effective and high throughput technique that uses electric field to provide sufficient tensile force to overcome the surface tension of a polymer fluid so that it can be ejected through an electrically charged needle to form fibers onto an electrically grounded collector [8]. Advantages of electrospun fibers are that they are flexible, lightweight,

ultra-long and has various thicknesses and shapes for applications in wearable or implantable devices [9]. Using an appropriate collector design, the one-dimensional fibers can be uniaxially aligned or randomly oriented to form a two-dimensional mat. As microstructures play a significant role in the performance of the fibers in devices, it is important to characterise the microstructures at various stages of heat treatment for the formation of ZnO from its polymer precursor. This work focused on the study of microstructural evolution experienced by the electrospun fibers under different calcination temperatures ranging from room temperature to 800 °C. XRD and FESEM equipped with EDX were employed to characterize the microstructures, morphologies, phases, dimensionality and chemistry of the nanostructures obtained while STA was used to monitor the thermal processes involved, such as changes in weight and heat exchange. The synthesized fibers were encapsulated and their piezoelectric performance was evaluated and compared by applying external mechanical forces to the fibers.

2. MATERIALS AND METHODS

A precursor solution was prepared by mixing 1.5 M zinc acetate ($Zn(CH_3COO)_2.2H_2O$) with 10% polyvinylpyrrolidone (PVP, Mw = 1300000) in ethanol at a volume ratio of 1:9. It was then loaded into a plastic syringe. A voltage of 16 kV was applied between the needle tip of the syringe and a rotating wire collector separated by a distance of 16 cm. Electrospinning was performed at a flow rate of 0.03 ml/min with rotating speed of the wire collector fixed at 600 rpm. The rotating wire collector allowed the formation of uniaxially aligned fibers. The as-synthesised zinc acetate/PVP composite fibers were then transferred to a silicon substrate and calcined at temperatures of 400 °C, 500 °C, 600 °C, 700 °C and 800 °C for 4 hours to form crystalline ZnO fibers, respectively. Both the PVP/zinc acetate and ZnO fibers were characterized using XRD (PANAlytical XPert Pro MPD), FESEM (Carl Zeiss Gemini SEM 500) equipped with EDX (Oxford Instrument) and STA (Netzsch 449F3 Jupiter).

3. RESULTS AND DISCUSSION

Fig. 1 shows a typical optical image of the aligned fibers electrospun at 16 kV. The average diameter of the as-spun fibers was found to be (125 ± 70) nm as determined digitally using the ImageJ software.

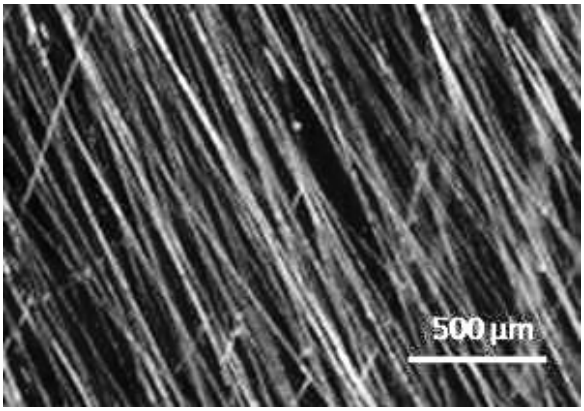

Fig. 1 Optical image of the aligned electrospun PVP/zinc acetate fibers

A fiber sample with initial weight of 14.9 mg was placed in an alumina pan and heated from 25 °C to 900 °C at a rate of 10 °C min under nitrogen purging of 50 ml/min. Fig. 2 shows the simultaneous TGA and DSC curves obtained during thermal process. The initial step of weight loss in the TGA curve was observed at 140 °C and continued till 320 °C. This was associated with an exothermic peak in the DSC curve in the same temperature range. This weight loss was attributed to sample dehydration and release of volatile PVP solvent. A major drop in weight was found at 460 °C, which was associated with burnt-out of organic components that constituted about 54% of the total weight of the sample. During this process, breakout of the organic bonds of the CH_3COO component of zinc acetate occurred. This was followed by the nucleation of

ZnO crystallites which was completed at 500 °C as may be evidenced from the intense exothermic peak observed in the same temperature range. With further increases in temperature, there was a gradual drop in weight and an associated exothermic peak. This was due to the occurrence of the second crystallization event, which was the formation of non-stoichiometric ZnO_x (x >1), as evidenced from the difference in percentage weight composition (from EDX analysis) between the fibers calcined at 800 °C (Zn: 53%; O: 47%) and those calcined at 700 °C or lower (Zn: 77%; O: 23%). Using X-ray photoelectron spectroscopy (XPS) as the characterization tool, Baek et al. [10] also observed that the process of calcination promoted the oxidation state of Zn species in their calcined electrospun ZnO fibers.

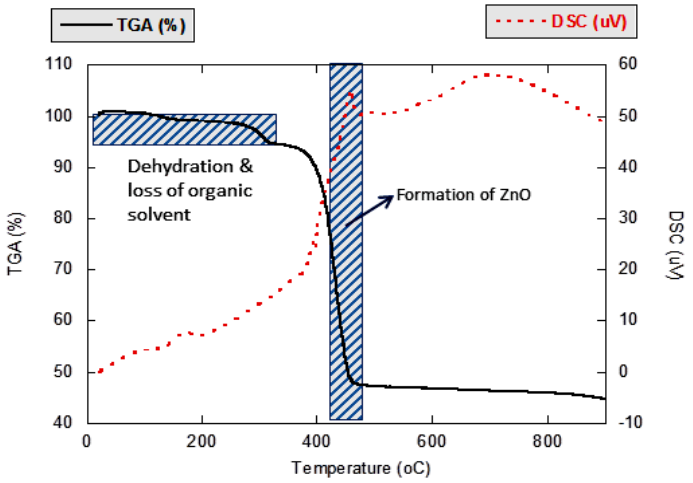

Fig. 2 DSC/TGA thermograms of the electrospun ZnO fibers

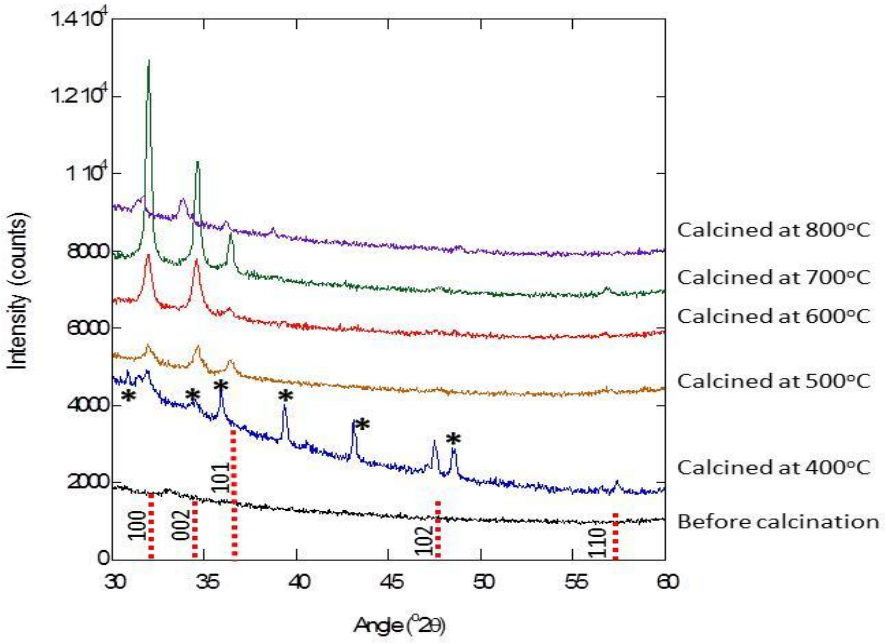

Fig. 3 Comparison of X-ray diffractograms of the electrospun ZnO fibers calcined at different temperatures. (The dotted stick pattern represents the peak positions of ZnO taken from JCPDS No: 00-001-1136 and * represents the peak positions of zinc acetate from JCPDS No.00-001-0089)

To evaluate the phase change in the sample, X-ray diffractograms of the electrospun fibers were obtained after heat treatment at different temperatures (Fig. 3). No characteristic peak of ZnO is observed for the fibers before heat treatment. With its polymeric components, the fibers were amorphous. After calcined at 400 °C, ZnO diffraction peaks start to emerge, with crystalline phase of zinc acetate coexisting in the sample. When calcination temperature was increased to 500 °C, the diffraction peaks of ZnO become more intense. Typical ZnO peaks of Miller indices 100, 002 and 101 of wurtzite crystal structure (JCPDS No: 00-001-1136) have been identified. After calcined at 800 °C, the diffraction peaks of ZnO are shifted to the positions of larger interplanar distances. The expansion of the lattice parameters is in accordance with the formation of non-stoichiometric ZnO_x (x >1).

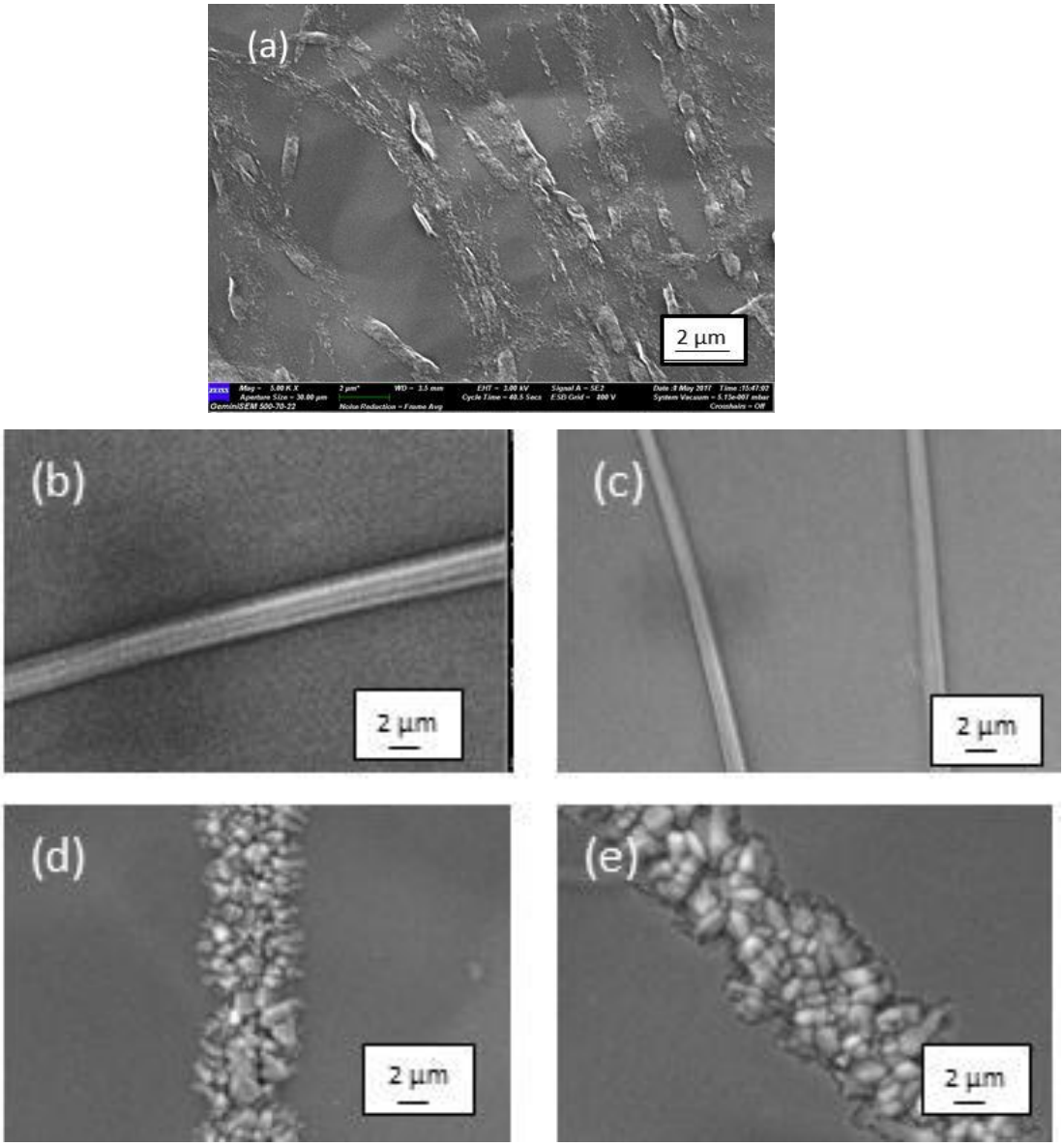

Fig. 4 FESEM images of electrospun ZnO fibers calcined at (a) 400 °C, (b) 500 °C, (c) 600 °C, (d) 700 °C and (e) 800 °C

Fig. 4 shows the microstructures of the fibers obtained at different calcination temperatures. After calcined at 400 °C, the fibers were found to be discontinuous due to the removal of majority polymer contents (Fig. 4a). When calcined at temperature of 500 °C or more, the fibers started to reconstruct to form continuous structures with the nucleation and growth of ZnO crystallites. At early stage of crystallization, partially hollow structures were formed, as shown by their tubular structure when calcined at 500 °C (Fig. 4b). Fibers calcined at 600 °C were, however, able to exhibit continuous solid structures (Fig. 4c). At 700 °C, the fibers were segmented into granular structure with microgaps between the grains and the sample no longer had a fibrous structure (Fig. 4d). Further heating of the samples produced larger ZnO grains, resulting from the merging of the grains, as well as branching of smaller ZnO nanorods from the granular cores to yield hierarchical structures (Fig. 4e).

To evaluate their piezo response, aligned ZnO fibers calcined at 600 °C were used. The fibers were transferred to a Kapton film by lift-off technique. Silver pastes were applied to both ends of the fibers as the Schottky electrodes for connection to an external circuit via a source measure unit (SMU) (Keithley 2600). A flexible PDMS layer was coated on the fibers. Fig. 5 shows the schematic diagram of the fabricated piezoelectric generator and the current pulse generated when the fibers were flexed by fingers.

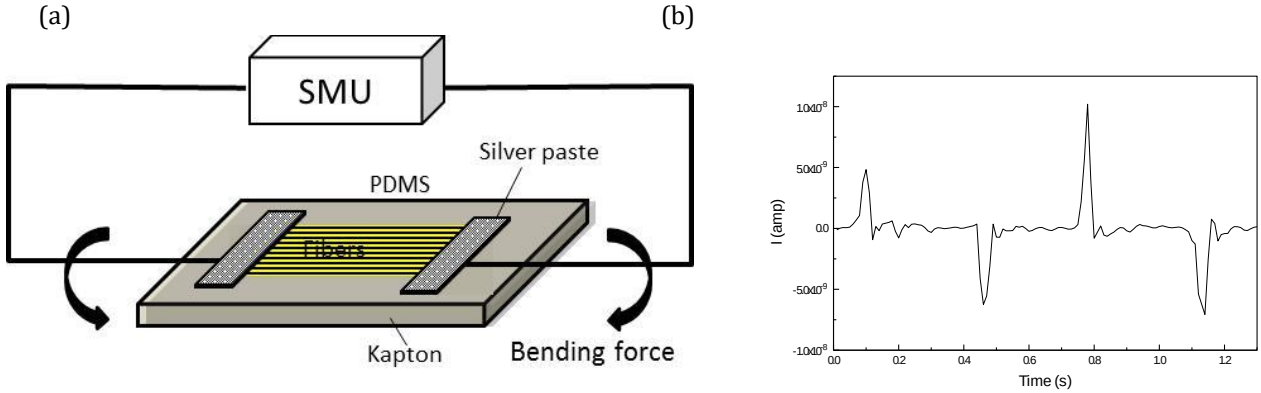

Fig 5 (a) Schematics of a ZnO piezo generator and (b) The current pulse produced when the fibers were bent and released

When the fibers were bent by external force, piezoelectric potential was created when the crystal symmetry was broken and electrons were driven from one electrode to another via the external circuit. Electrons were also accumulated at the interface between the fibers and the electrode. When the force was released, the piezo potential disappeared and the accumulated electrons were then flown back in the opposite direction, generating a negative pulse. A current pulse was thus generated by applying and releasing the force. A.C. pulse was generated and a maximum output current pulse of 10 nA was demonstrated for an approximate effective working area of 1 cm^2 of fibers. The presence of Schottky contact was important to enhance the output signal from the generator to be above the noise level by preventing the electrons to flow into the ZnO fibers through the interface [11].

4. SUMMARY

ZnO fibers calcined at different temperatures showed different microstructures and morphologies. Continuous single-phase ZnO fibers started to form at a temperature around 460 °C and evolved through various stages of microstructural formation from tubular-like structures to segmentation of granular structures and hierarchical structures. The ZnO fibers also experienced a stoichiometry change when heated to 800 °C. Continuous ZnO fibres calcined at 600 °C have been demonstrated to be able to generate a maximum current pulse of 10 nA cm^{-2} when mechanically bent.

ACKNOWLEDGEMENT

The authors would like to acknowledge Malaysian Nuclear Ageny for supporting this work under the project NM-R&D-16-01. This work is also partially funded by project grant #FRGS/ST01(01)/1208/2014(09).

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