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Fabrication of zinc titanate nanofibers by electrospinning technique

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ABSTRACT

The zinc titanate composite nanofibers were prepared using electrospinning method combining sol–gel process followed by calcining the precursor PVP/$Zn(CH_3COO)_2$–$Ti(OC_4H_9)_4$ fibers under air in the temperature range of 400–700 °C. The nanofibers were characterized by thermal field emission scanning electron microscope (FE-SEM), X-ray diffraction (XRD), thermal gravimetric and differential thermal analysis (TG–DTA). FE-SEM micrographs indicated that the surfaces of the nanofibers are uniform and smooth and the diameter of the fiber decreasing as the calcination temperature increasing. It is also found that ZnO–TiO_2 ceramic fibers including $ZnTiO_3$, Zn_2TiO_4 and rutile phase were synthesized by calcining the precursor PVP/$Zn(CH_3COO)_2$–$Ti(OC_4H_9)_4$ composite fibers at 700 °C.

1. Introduction

Zinc titanates have been investigated for applications in many fields such as paint pigment, gas sensor and catalytic sorbent in recent years [1–3]. It is reported that there are three compounds existing in the ZnO–TiO_2 system including Zn_2TiO_4 (cubic), $ZnTiO_3$ (hexagonal), and $Zn_2Ti_3O_8$ (cubic) [4]. Among these compounds, ilmenite type hexagonal $ZnTiO_3$ based ceramic has been reported to have superior electrical properties, which could be used as microwave resonator, gas sensor and paint pigment. $ZnTiO_3$ decomposes into Zn_2TiO_4 and rutile roughly at 925 ± 25 °C under the condition of solid-state dry reactions and therefore is considered to be a metastable phase. Zn_2TiO_4 is stable phase from room temperature to its liquid temperature and can easily be prepared by conventional solid-state reaction between 2ZnO and 1TiO_2 in mole ratio [5,6]. However, synthesis of $ZnTiO_3$ from 1ZnO and 1TiO_2 by solid-state reaction method is very difficult because it tends to decompose into Zn_2TiO_4 and rutile during solid-state reaction process. Since the synthesis process is affected by many factors such as the preparation method, the ratio of Zn to Ti, etc. Therefore, it is still a challenge to synthesis ZnO–TiO_2. Various synthesis methods were reported in recent years, such as solid-state reaction method [3,4], sol–gel process [6] and molten salt synthesis [7], etc.

Nanostructured materials have exhibited novel physical and chemical properties that can be used in optics, data-storage devices and nanoelectronic devices [1,8]. As a type of nanostructure with specific morphologies, nanofiber has been studied actively as a new functional material. Nanofiber is a fiber with a diameter of nanometer order less than 1 μm, and the aspect ratio more than 100. Nanofiber fabric has large specific surface area and nano-sized effect [8–10]. In order to obtain nanofiber materials, various preparation methods have been developed [11–13]. Among many available methods for producing nanofiber, the electrospinning is a very simple and convenient method for fabricating organic and inorganic nanofibers with long lengths, uniform diameters and various compositions [13–17].

In this work, PVP/ZnO–TiO_2 nanofibers were fabricated by electrospinning and ZnO–TiO_2 nanofibers were obtained by calcination of the composite fibers. The change in morphologies of ZnO–TiO_2 nanofibers with the calcination temperature was systematically investigated to elucidate the synthesis mechanism by using FE-SEM, TG–DTA and XRD.

2. Experimental

All reagents used in the experiments were of analytical grade without further purification. The typical spinning solution was prepared by the following procedures. Based on a sol–gel method, 0.01 mol $Ti(OC_4H_9)_4$ and isometric acetic acid were mixed with 8 g polyvinyl pyrrolidone (PVP) ($M_r \approx 1000$) powders and 30 ml ethanol under vigorous stirring for 20 min. Then stoichiometric $Zn(CH_3COO)_2$ (Zn/Ti = 2:1) was added to the solution by sufficiently stirring for 3 h to obtain a homogeneous solution. After drying, a transparent viscous precursor sol of PVP/$Zn(CH_3COO)_2$–$Ti(OC_4H_9)_4$ was obtained [16].

Then the PVP/ZnO–TiO_2 nanofibers were obtained by electrospinning method. The electrospinning setup was shown in Fig. 1. The above precursor sol was loaded into a glass syringe with a stainless needle, which acted as anode. A grounded aluminum foil served as counter electrode and collector, and the distance of the needle tip and the collector was fixed to 20 cm. When a high voltage (20 kV in this work) was applied, the composite fibers were obtained on the aluminum foil. Finally, the fibers were heated at 400, 550 and 700 °C for 1 h in air respectively to remove the organic material and ZnO–TiO_2 nanofibers were obtained.

The thermal decomposition behavior of precursor xerogel was examined on a thermal analysis system (NETZSCH STA-499C, NETZSCH, Germany) under an ambient atmosphere in the temperature range from 30 to 1000 °C at a heating rate of

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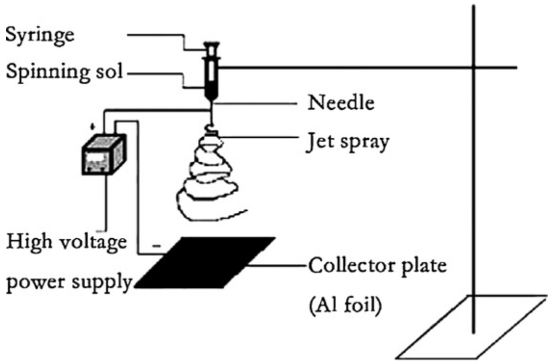

Fig. 1. Schematic diagram of single needle electrospinning setup.

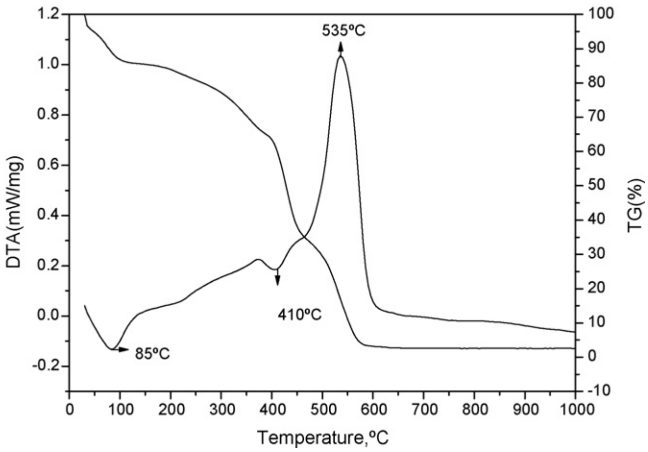

Fig. 2. TG–DTA analyze of the precursor xerogel of ZnO–TiO_2 nanofibers.

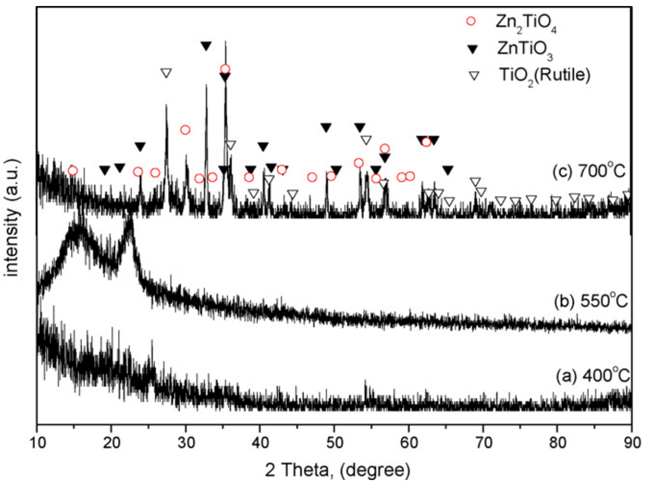

Fig. 3. (a–c) XRD of PVP/$Zn(CH_3COO)_2$–$Ti(OC_4H_9)_4$ fibers calcined at different temperatures.

10 °C/min with Al_2O_3 powder as a reference. Phase analyses were carried out on a 21 kW extra-power powder XRD (Model: M21XVHF22, Mac Science, Yokohama, Japan) at room temperature using Cu Kα radiation. The morphologies of nanofibers were investigated using thermal field emission scanning electron microscope (FE-SEM) (Model: SUPRA^{TM} 55, ZEISS Co., Germany).

3. Results and discussion

Fig. 2 shows the thermal behavior of precursor xerogel. Three distinct stages of mass loss could be noticed in the TG curve. The first stage is 30–120 °C and at this stage the weight loss is about 14%. During this stage, a small endothermic peak appeared at about 85 °C as shown in DTA curve, which indicated the loss of solvent such as water and ethanol in the composite sol. At the second stage, i.e., 120–455 °C, the weight loss was about 50% and a smaller endother-

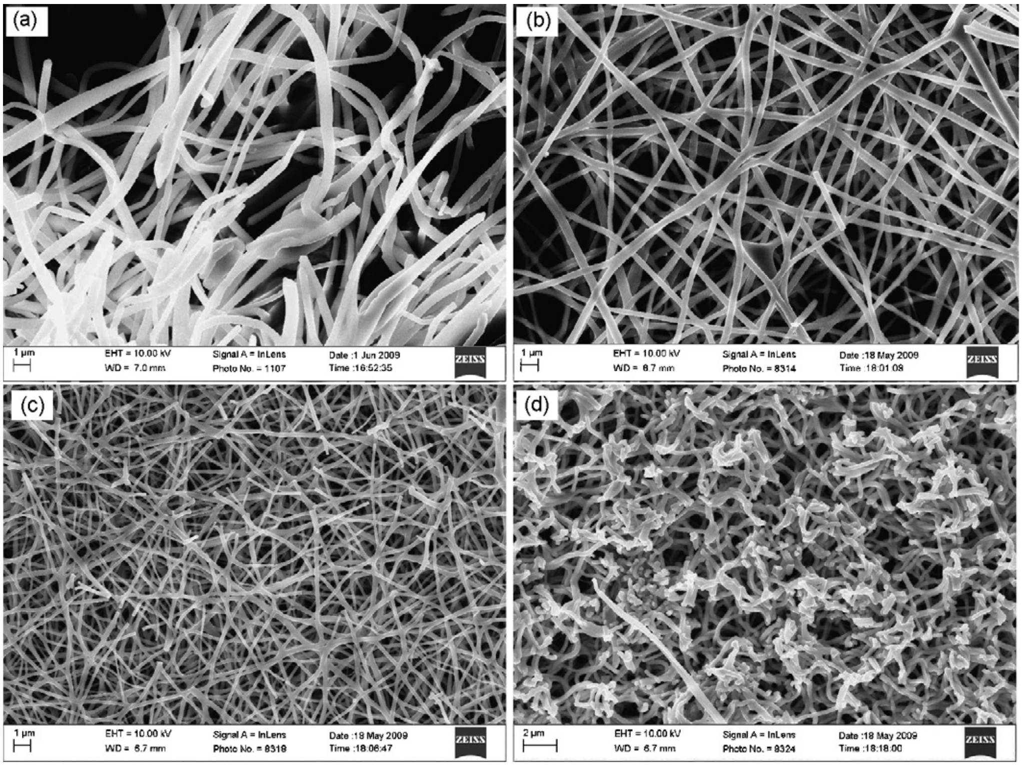

Fig. 4. FE-SEM of PVP/$Zn(CH_3COO)_2$–$Ti(OC_4H_9)_4$ fibers and calcined at different temperatures: (a) PVP/$Zn(CH_3COO)_2$–$Ti(OC_4H_9)_4$ composite fibers; (b) 400 °C; (c) 550 °C; (d) 700 °C.

mic peak near 410 °C in DTA curve was observed, which attributed to the degradation of PVP and the formation of ZnO and TiO_2 [8,14]. At the last stage, i.e., 455–550 °C, the weight loss was about 33.4% and a sharp exothermic peak appeared at 535 °C, which was possibly caused by the combustion of organic materials. Both the TG and DTA curves became stable after 600 °C, indicating that water, ethanol and organic compounds in the xerogel volatilize have completely been removed.

The XRD patterns of $PVP/Zn(CH_3COO)_2–Ti(OC_4H_9)_4$ composite fibers calcined at different temperatures are shown in Fig. 3. It can be seen that the xerogel fibers have no peaks appeared when calcined at 400 °C, and only have two broad peak around 15° and 22° when calcined at 550 °C. This revealed that the composite fibers were amorphous state in structure, which was in accordance with the results of the TG–DTA curves. Therefore $ZnO–TiO_2$ fibers could be obtained after 550 °C. When the composite fibers were calcined at 700 °C (Fig. 3(c)), the characteristic peaks of $ZnTiO_3$, Zn_2TiO_4 and rutile formed by combustion of organic component. Because the low calcination temperature (700 °C) and the short soaking time (1 h), the chemical reaction was incomplete and the main crystal phase composed of $ZnTiO_3$, Zn_2TiO_4 and rutile as seen in Fig. 3(c).

Morphologies of as-prepared nanofibers before and after calcination at different temperatures were characterized by FE-SEM. The surface morphology and size of the samples varied strongly depending on the calcinations temperature as shown in Fig. 4. The surface of as spun randomly oriented composite fibers appeared to be relatively smooth and uniform due to the amorphous nature of the $PVP/Zn(CH_3COO)_2–Ti(OC_4H_9)_4$ fibers. The lengths can reach several micrometers and the diameter range from 400 to 800 nm as shown in Fig. 4(a). The diameter of the fibers shrank drastically to 150–300 nm because of the evaporation of water or decomposition of PVP, $Zn(CH_3COO)_2$ or $Ti(OC_4H_9)_4$ after calcination as shown in Fig. 4(b)–(d). The network structure still retained during the annealing process, but a change in fiber morphology was observed after increasing temperature to 700 °C. The fibers were broken up and became bending and the surface became rough illustrated in Fig. 4(d), which caused by the burn out of PVP and crystallization and coalescence of the grains [18]. Hence, the multi-component ceramics fibers can be prepared by sol–gel assisted electrospinning technique.

4. Conclusions

$PVP/Zn(CH_3COO)_2–Ti(OC_4H_9)_4$ composite nanofibers were fabricated by combining sol–gel process and electrospinning technique. The composite nanofibers were calcined under air in the temperature range of 400–700 °C and the zinc titanate nanofibers were obtained. The reaction process of the composite nanofibers was investigated by TG–DTA, which indicated that there were three steps during the process and $ZnO–TiO_2$ fibers could be obtained after 550 °C. At relatively low temperatures (below 550 °C), the $ZnO–TiO_2$ composite nanofibers existed in amorphous state and the surface morphology and size of the samples decreased with temperature increasing. When the temperature increased to 700 °C, the $ZnO–TiO_2$ ceramic fibers was synthesized composing of $ZnTiO_3$, Zn_2TiO_4 and rutile phase.

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