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Preparation and Characterization of Tetracomponent $ZnO/SiO_2/SnO_2/TiO_2$ Composite Nanofibers by Electrospinning

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ABSTRACT

$[Zn(CH_3COO)_2 + PVP]/[C_2H_5O)_4Si + PVP]/[SnCl_4 + PVP]/[Ti(OC_4H_9)_4 + CH_3COOH + PVP]$ precursor composite fibers have been fabricated through self-made electrospinning equipment via electrospinning technique. $ZnO/SiO_2/SnO_2/TiO_2$ composite nanofibers were obtained by calcination of the relevant precursor composite fibers. The samples were characterized by thermogravimetric-differential thermal analysis (TG-DTA), X-ray diffractometry (XRD), Fourier transform infrared spectroscopy (FTIR), and Scanning electron microscopy (SEM). TG-DTA analysis reveals that solvents, organic compounds and inorganic in the precursor composite fibers are decomposed and volatilized totally, and the mass of the samples kept constant when sintering temperature was above 900˚C, and the total mass loss percentage is 88%. XRD results show that the precursor composite fibers are amorphous in structure, and pure phase $ZnO/SiO_2/SnO_2/TiO_2$ composite nanofibers are obtained by calcination of the relevant precursor composite fibers. FTIR analysis manifests that pure inorganic oxides are formed. SEM analysis indicates that the width of the precursor composite fibers is ca. 1.485 ± 0.043 μm. The width of the $ZnO/SiO_2/SnO_2/TiO_2$ composite nanofibers is *ca.* 1145.098 ± 68.093 nm.

Keywords: $ZnO/SiO_2/SnO_2/TiO_2$; Tetracomponent; Composite Nanofibers; Electrospinning

1. Introduction

One-dimensional nanomaterials, such as nanofibers, nanowires, nanobelts, nanoribbons, and nanorods, are a new class of nanomaterials that have been attracting a great research interest in the last few years. These materials have been demonstrated to exhibit superior optical, acoustic, electrical, magnetic, thermal, and mechanical properties, and thus, can be used as both interconnects and functional components in the fabrication of nanoscale electronic and optoelectronic devices. Electrospinning technique as a simple, convenient, and versatile method has been utilized in the preparation of many one-dimensional nanostructural materials such as long fibers with diameters ranging from tens of nanometers up to micrometers [1]. It has been used to produce variety of materials, such as rare earth oxyfluoride [2], GGG: Eu^{3+} nanobelts [3], TiO_2 nanobelts [4], PANI nanobelts [5], three mixed oxides(Co_3O_4,CuO, and MnO_2) nanobelts [6] and TiO_2@SiO_2 nanocables [7] through electrospinning technique. Recently, this technique was used as an approach to fabricate composite nanofibers. For example, Zhang, *et al.* [8] synthesized SnO_2/TiO_2 composite nanofibers through electrospinning technique. However, to the best of our knowledge, there have been no reports on the preparation of $ZnO/SiO_2/SnO_2/TiO_2$ composite nanofibers by electrospinning technique. Synthesis of composite nanofibers materials with unique optical, electronic, magnetic, and catalytic properties, which are fundamentally important and technologically useful. In this paper, $ZnO/SiO_2/SnO_2/TiO_2$ composite nanofibers were fabricated by calcination of the electrospun $[Zn(CH_3COO)_2 + PVP]/[C_2H_5O)_4Si + PVP]/[SnCl_4 + PVP]/[Ti(OC_4H_9)_4 + CH_3COOH + PVP]$ precursor composite fibers, and some new results were obtained and this preparation technique can be applied to prepare other composite nanofibers.

2. Experimental Section

2.1. Chemicals

Polyvinyl pyrrolidone (PVP) (Mw = 1,300,000, AR), ethanol (CH_3CH_2OH), butyl titanate ($Ti(OC_4H_9)_4$), zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$), stannic chloride ($SnCl_4 \cdot 5H_2O$), tetraethyl orthosilicate ($(C_2H_5O)_4Si$), acetic acid (CH_3COOH) and N,N-dimethylformamide (DMF, AR) were bought from Tiantai Chemical Co. Ltd., All chemicals were analytically pure and directly used as received without further purification.

2.2. Preparation of Precursor Composite Sol

2.4 g of PVP powders and 1.8 g of $Zn(CH_3COO)_2{\cdot}2H_2O$ were dissolved in 16 g of DMF, and stirred at room temperature for 10 h. The above sol was placed in an airtight container for about 5 h, and then, transparent viscous sol of [$Zn(CH_3COO)_2$ + DMF + PVP] was obtained; 2.5 g of PVP powders and 5 ml of $(C_2H_5O)_4Si$ were dissolved in10 ml of CH_3CH_2OH, and stirred at room temperature for 10 h. The above sol was placed in an airtight container for about 5 h, and then, transparent viscous sol of [$(C_2H_5O)_4Si$ + CH_3CH_2OH + PVP] was obtained; 2.5 g of PVP powders and 1.8 g of $SnCl_4{\cdot}5H_2O$ were dissolved in 20 ml of DMF, and stirred at room temperature for 10 h. The above sol was placed in an airtight container for about 5 h, and then, transparent viscous sol of [$SnCl_4$ + DMF + PVP] was obtained; 2.0405 g of PVP powders and 17 ml of CH_3CH_2OH and 3 ml of CH_3COOH were dissolved in 5 ml of $Ti(OC_4H_9)_4$, and stirred at room temperature for 10 h. The above sol was placed in an airtight container for about 5 h, and then, transparent viscous sol of [$Ti(OC_4H_9)_4$ + CH_3CH_2OH + CH_3COOH + PVP] was obtained.

2.3. Characterization Methods

XRD analysis was performed on a Holland Philip Analytical PW1710 BASED X-ray diffractometer using Cu $K\alpha_1$ radiation, with the working current and voltage at 30 mA and 40 kV, respectively. Scans were made from 10˚ to 90˚ at the speed of 4 (˚)/min, and the step was 0.02˚. The morphology and size of the samples were observed with an S-4200 scanning electron microscope made by Japanese Hitachi Company. TG-DTA analysis was carried out on an SDT-2960 thermal analyzer made by American TA instrument company in atmosphere, and the temperature rising rate was 10˚C/min. FTIR spectra of the samples were recorded on BRUKER Vertex 70 Fourier transform infrared spectrophotometer made by Germany Bruker company, and the specimen for the measurement was prepared by mixing the samples with KBr powders and then the mixture was pressed into pellets, the spectrum was acquired in a wave number range from 4000 cm^{-1} to 400 cm^{-1} with a resolution of 4 cm^{-1}.

2.4. Preparation of $ZnO/SiO_2/SnO_2/TiO_2$ Composite Nanofibers

Schematic diagram of electrospinning setup was shown in **Figure 1**. The above precursor sol were placed in four focusing syringes and delivered at a constant flow rate using plastic capillaries. The anodes were placed in the sol, and a grounded aluminum foil served as counter electrode and collector. When a high voltage (26 kV in this work) was applied, and the distance between the capillary tip and the collector was fixed to 18 cm, a dense web of [$Zn(CH_3COO)_2$ + PVP]/[$C_2H_5O)_4Si$ + PVP]/[$SnCl_4$ + PVP]/[$Ti(OC_4H_9)_4$ + CH_3COOH + PVP] precursor composite fibers were collected on the aluminum foil. These fibers were calcinated at a rate of 1˚C/min and remained for 8 h at 900˚C, respectively. Thus, $ZnO/SiO_2/$ SnO_2/TiO_2 composite nanofibers were obtained.

3. Results and Discussion

3.1. TG-DTA Analysis

Figure 2 shows the thermal behavior of precursor composite fibers. The weight loss was involved in four stages in TG curve. The first weight loss is 19% in the range of 40˚C to 277˚C accompanied by a small endothermic peak near 83˚C in the DTA curve, which is caused by the loss of the surface absorbed water or the residual water molecules in the precursor composite fibers. The second weight loss step (27%) is between 277˚C and 340˚C accompanied by an exothermic peak near 330˚C in the DTA curve because of the decomposition of the $Ti(OC_4H_9)_4$, CH_3COOH and side-chain of PVP. The third weight loss (36%) in the TG curve (340˚C - 503˚C) was possibly corresponded to the decomposition of $SnCl_4{\cdot}5H_2O$, Zn $(CH_3COO)_2{\cdot}2H_2O$ [9], $(C_2H_5O)_4Si$ [10] and main-chain of PVP. In the DTA curve, an exothermic peak was located at 470˚C. The last weight loss is 6% in the temperature change from 503˚C to 900˚C. In the DTA curve a sharp exothermic peak is located at 574˚C. This is likely to be the totally oxidation combustion of the inorganic salts. And above 900˚C, the TG and DTA curves were all unvaried, indicating that water, organic compounds and inorganic salts in the precursor composite fibers were completely volatilized and pure $ZnO/SiO_2/$ SnO_2/TiO_2 composite nanofibers could be obtained above

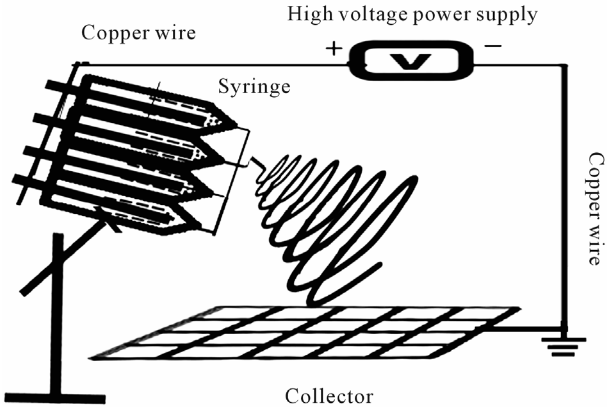

Figure 1. Schematic diagram of electrospinning setup for preparation of composite nanofibers.

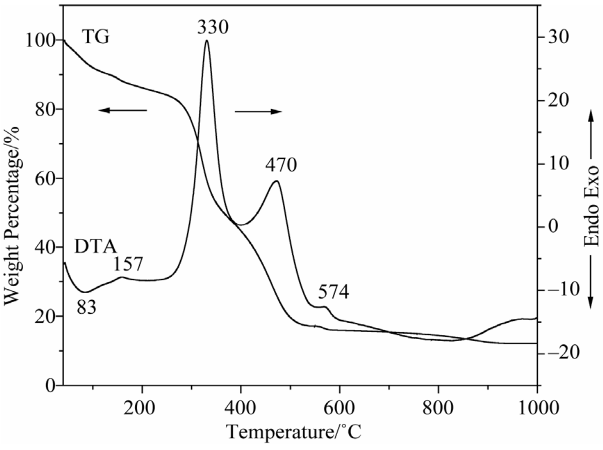

Figure 2. TG-DTA curves of precursor composite fibers.

900˚C. The total weight loss was 88%.

3.2. XRD Analysis

In order to investigate the variety of phase, the precursor composite fibers and samples obtained after being calcined at 900˚C were characterized by XRD, as indicated in **Figure 3**. Precursor composite fibers (**Figure 3(a)**) only have a broad peak around 20˚, which is the typical peak of the polymer [11]. This revealed that precursor composite fibers were amorphous in structure. From **Figure 3(b)**, XRD patterns displayed some new diffraction peaks when calcined at 900˚C, and meanwhile, the diffraction peak of precursor composite material disappeared, indicating that PVP was decomposed and removed out from precursor composite nanofibers, observed reflections were indexed to (110), (101), (200), (220) and (301) of TiO_2, and the *d* values and relative intensity of the peaks are consistent with those of JCPDS standard card (21 - 1276), indicating that the prepared TiO_2 is tetragonal in structure with space group $P4_2$/mnm; and observed reflections can be indexed to (220) and (311) of SnO_2, and the *d* values and relative intensity of the peaks are consistent with those of JCPDS standard card (33 - 1374), indicating that the prepared SnO_2 is cubic in structure with space group Fm3m; and observed reflections were indexed to (110), (002), (102) and (301) of ZnO, and the *d* values and relative intensity of the peaks are consistent with those of JCPDS standard card (36 - 1451), indicating that the prepared ZnO is hexagonal in structure with space group P63mc; As can be seen from **Figure 3(b)** have a broad peak around 22˚, which is the typical peak of the SiO_2 amorphous in structure. Therefore, $ZnO/SiO_2/SnO_2/TiO_2$ composite nanofibers with stable phase can be prepared at 900˚C.

3.3. FTIR Spectra Analysis

The formation of the $[Zn(CH_3COO)_2 + PVP]/[C_2H_5O)_4Si + PVP]/[SnCl_4 + PVP]/[Ti(OC_4H_9)_4 + CH_3COOH + PVP]$ precursor composite fibers and samples calcined at 900˚C for 8 h is further supported by the FTIR spectra in **Figure 4**. As seen form **Figure 4(a)**, the FTIR spectrum of precursor composite fibers indicated that the wide absorption peak at 3422 cm^{-1} attributes to the stretching vibrations of O-H of the surface absorbed water. The absorption peaks at 2966 cm^{-1}, 1645 cm^{-1}, 1474 cm^{-1} and 1302 cm^{-1} corresponding to the stretching vibrations of C-H, C=O, C-N and C-C bond in PVP [12]. It can be seen from **Figure 4(b)** (900˚C) that the wide absorption peak at 3462 cm^{-1} and 1645 cm^{-1} of the surface absorbed water became weaker and all peaks of PVP disappeared. At the same time, four new absorption peaks at low wavenumber are appeared, the wide absorption peak at 1088 cm^{-1}, which ascribe to the vibration of Si-O-Si

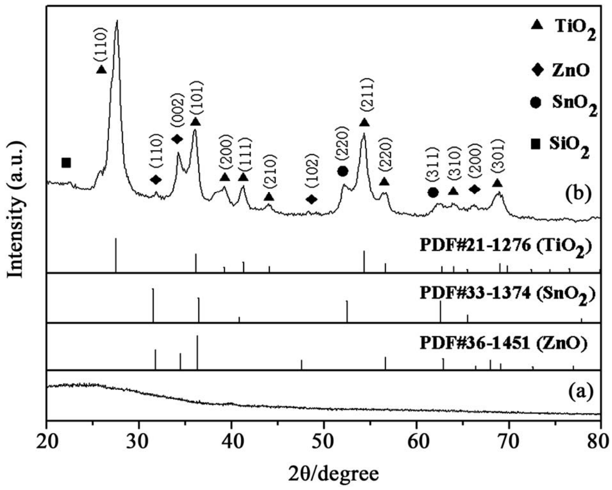

Figure 3. XRD patterns of the precursor composite fibers (a) and samples calcined at 900˚C for 8 h (b).

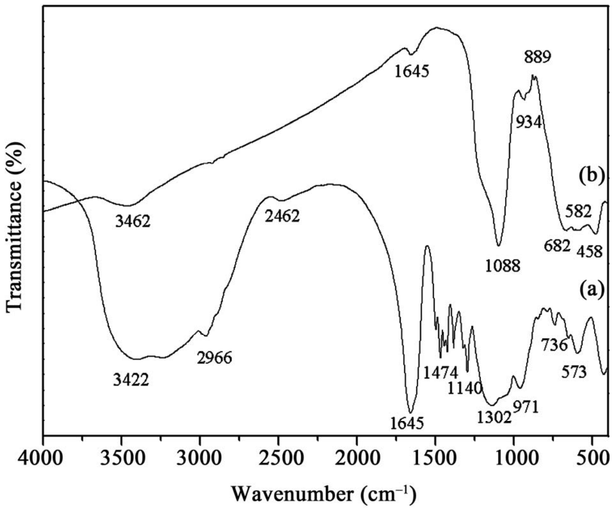

Figure 4. FTIR spectra of the precursor composite fibers (a) and samples calcined at 900˚C for 8 h (b).

bonds, the wide absorption peak at 934 cm^{-1}, which ascribe to the vibration of Si-OH bond, the wide absorption peak at 458 cm^{-1}, 582 cm^{-1} and 682 cm^{-1} which ascribe to the vibration of Ti-O-Ti bonds, Sn-O-Sn bond and Zn-O bonds, indicating that the formation of $ZnO/SiO_2/SnO_2/TiO_2$ composite nanofibers. The results of FTIR analysis were in good agreement with XRD results.

3.4. SEM Analysis

The morphology of the precursor composite fibers and $ZnO/SiO_2/SnO_2/TiO_2$ composite nanofibers were investigated by SEM analysis (The width values of the samples are tested by softwares of Ipwin32 and Origin8). As seen from **Figures 5(a)** and **(b)**, the surface of the precursor composite fibers is very smooth. The width of the precursor composite fibers is ca. 1.485 ± 0.043 μm. As seen from **Figures 5(c)** and **(d)** the surface of $ZnO/SiO_2/SnO_2/TiO_2$ composite nanofibers became coarser. The width of composite nanofibers is *ca.* 1145.098 ± 68.093 nm.

3.5. EDS Analysis

To determine the composite nanofibers component further, energy dispersive spectroscopy (EDS) of the samples was performed. The EDS analysis results revealed that by calcining the precursor composite fibers (**Figure 6(a)**) at 900˚C for 8 h the $ZnO/SiO_2/SnO_2/TiO_2$ composite nanofibers (**Figure 6(b)**) are only composed of Ti, Sn, Zn, Si and O elements. The results of EDS analysis were in good agreement with the above results.

4. Conclusions

$[Zn(CH_3COO)_2 + PVP]/[C_2H_5O)_4Si + PVP]/[SnCl_4 + PVP]/[Ti(OC_4H_9)_4 + CH_3COOH + PVP]$ precursor composite fibers were successfully fabricated using an electrospinning technique, and $ZnO/SiO_2/SnO_2/TiO_2$ composite nanofibers were synthesized by calcining the precursor composite fibers at 900˚C for 8 h. TG-DTA and FTIR revealed that the formation of $ZnO/SiO_2/SnO_2/TiO_2$ composite nanofibers was largely influenced by the calcination temperatures. SEM micrographs indicated that the surface of the precursor composite fibers was smooth and became coarse with the increase of calcination temperatures. EDS analysis results revealed that $ZnO/SiO_2/SnO_2/TiO_2$ composite nanofibers were only composed of Ti, Sn, Zn, Si and O elements.

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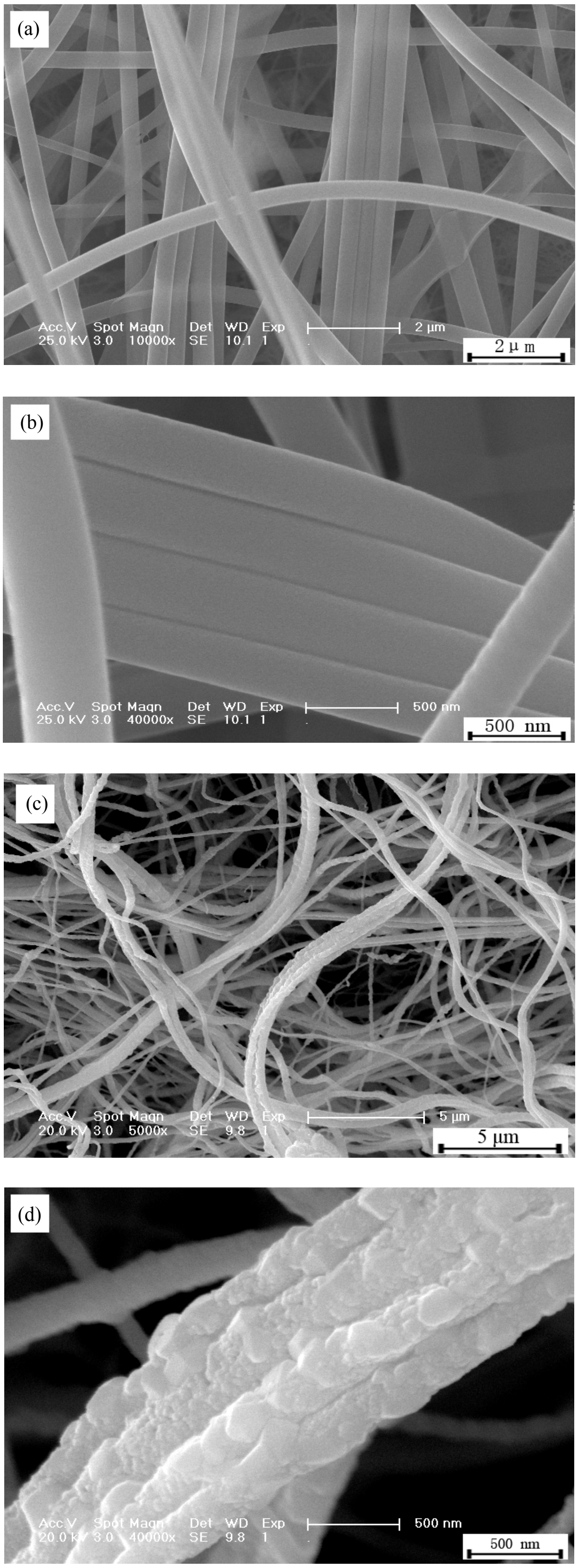
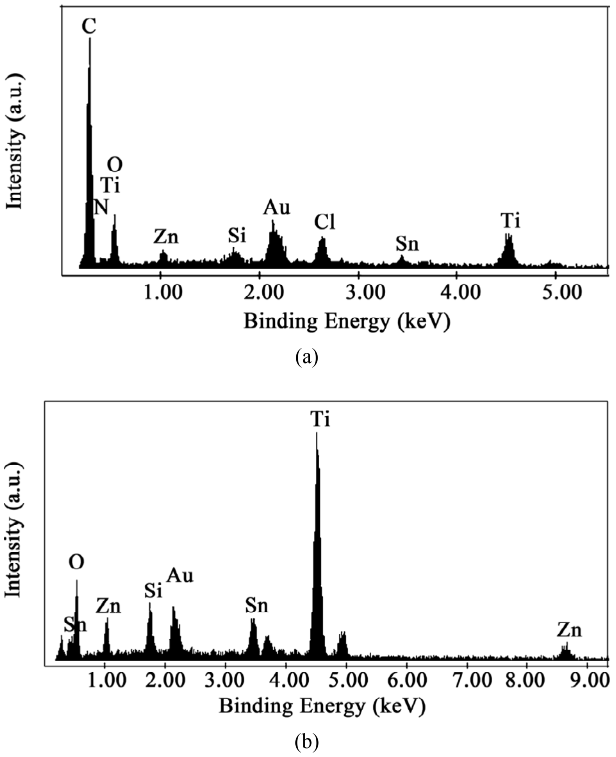


Figure 5. SEM images of the precursor composite fibers ((a)-(b)) and samples calcined at 900˚C for 8 h ((c)-(d)).



(a)

(b)

Figure 6. EDS images of the precursor composite fibers (a) and samples calcined at 900˚C for 8 h (b).

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