Electrospinning Preparation and Infrared-Emissivity Properties of Zn$_{1-x}$Co$_x$O Nanofibers

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Abstract. Wurtzite-type Zn$_{1-x}$Co$_x$O nanofibers were successfully fabricated by sol-gel method combined with electrospinning technology. The as-prepared fiber samples were characterized by TGA-DSC, XRD, FTIR and SEM techniques. The infrared emissivity of the product were tested using an IR-2 infrared emissivity analyzer. The results show that wurtzite structure is formed at 600°C for 2h. These nanofibers have diameters in the range of 60-100nm. As the doping concentration increases, The infrared emissivity of the sample decreases first and then increases slowly. When $x = 0.04$, the lowest infrared emissivity is 0.76. This makes Zn$_{1-x}$Co$_x$O nanofibers have a good prospect in the infrared emissivity nanomaterials.

1. Introduction
In recent years, with the rapid development of infrared detection system and the improvement of detection accuracy, military equipments and facilities are under great threat, especially fighters, tanks and ships with high-power engines. When their engines are running in operation, they produce high and radiation, which greatly increases the possibility of exposure to the infrared detection devices. Therefore, the research of infrared stealth materials has attracted the attention of the world's military powers[1].

Zinc oxide (ZnO) is one of the most important n-type semiconductor materials with a direct wide bandgap of 3.37eV at room temperature[2,3]. It exhibits many excellent properties, such as, good chemical stability, low cost, unique optical, and electrical properties. Therefore, ZnO has a wide range of applications in the field of optoelectronic devices[4], light catalytic[5], sensors[6] and so on. In recent years, ZnO and ZnO-based composites have attracted increasing interest due to its remarkable low infrared emissivity. Ye Xiaoyun et al[7] prepared ZnO particles with different microstructures by hydrothermal method. Influence of particle morphology on the infrared emissivity was studied. The results show that all the samples possess good crystallinity with hexagonal wurtzite structure. The infrared emissivity values of rod-like and bundle-like ZnO are lower than that of spherical ZnO. The infrared emissivity value of flower-like ZnO is relatively lower, with a value of 0.673. This shows that the morphology of the materials has an important influence on the infrared emissivity.

The nanofibers have different properties from bulk materials in electronic transportation, optics, magnetism, electricity and catalysis because of their high aspect ratio, specific surface area and unique morphology[8]. In addition, due to the small-scale effect, nanofibers have oscillatory properties at low frequencies. Based on this phenomenon, nanofibers are good absorbing materials, and become widely used in camouflage, concealment and other military fields[9]. Therefore, research and preparation of doped semiconductor nanofibers is of great significance.
The traditional preparation methods of micro-nanofibers include spinning method\cite{10}, template synthesis method\cite{11}, phase separation method\cite{12} and self-assembly method\cite{13}. Electrospinning method\cite{14} is a kind of processing technology by using polymer solution or melt in the strong electric field. Compared with the traditionally fiber, the diameter of the fiber prepared this way is usually 10 nanometers to a few microns, which is one of the effective methods to obtain the nanometer sized long fiber with high specific surface area. And the process is simple. The advantage of the sol-gel method is that the components of the sample are mixed uniformly, which is very favorable to the synthesis of the doped samples. Based on the advantages above, Zn$_{1-x}$Co$_x$O fibers are synthesized by electrospinning technology combined with sol-gel method.

In this study, Zn$_{1-x}$Co$_x$O fibers with nano structure are firstly synthesized by electrospinning technology combined with sol-gel method. And the microstructure, morphology, synthesis process and the infrared emissivity of Zn$_{1-x}$Co$_x$O are studied systematically.

2. Experimental

Synthesis of Electrospun Nanofibers

(CH$_3$COO)$_2$Zn·2H$_2$O and Co(NO$_3$)$_2$·6H$_2$O used for the preparation of Zn$_{1-x}$Co$_x$O nanofibers in accordance with the stoichiometry of Zn$_{1-x}$Co$_x$O respectively. All of the raw materials were dissolved in distilled water and stirred until they were completely dissolved. Firstly, a small amount of citric acid was added into the solution, and then NH$_3$·H$_2$O was added to adjust the solution to pH=8.0 or so. After that, the mixed solution was stirred for 16h at room temperature continuously. Then the solution was put at 80°C to evaporate water until the formation of viscous sol.

A PVP solution of 15wt% was prepared by dissolving PVP powder in glacial acetic acid and stirring for 4h. Taking a certain amount of the sol to add to the solution and stirring it fully, then the spinning precursor solution was made. Precursor nanofibers were prepared by using electrospinning technology. The conditions of electrospinning were at the voltage of 20kV, the needle of which is the23G stainless steel, and the distance between the needle and receiving plate is 20cm.

The precursor nanofibers after drying were calcined at 600°C for 2h respectively with the heating rate of 2°C/min, and then cooled to room temperature with the furnace.

Sample Characterization and Infrared Emissivity Measurement

The synthesis process were studied by Differential thermal-thermogravimetric analyzer (SDT-Q600, American). The crystallographic structure of the spun and calcined nanofibers were characterized by X-ray diffraction analysis (X6, Puxi, Beijing) with Cu Kα radiation (λ=0.15406nm). The infrared spectrograms of samples were studied by infrared spectrometer, FTIR (Nicolet-380, American). The morphologies of samples were studied by scanning electron microscopy, SEM (S-4800, Japan and KYKY-600, Beijing). The infrared emissivity of sample was studied by IR-2 infrared-emissivity analyzer (IR-2, Shanghai).

3. Results and discussion

3.1 Samples Characterization

The TGA curve of Zn$_{0.96}$Co$_{0.04}$O/PVP precursor nanofibers are shown in Figure 1. The thermal decomposition process of precursor fibers can be roughly divided into four stages as follows. The thermal decomposition process of precursor fibers can be roughly divided into four stages as follows. Stage 1 is from room temperature to 150°C, a weight loss step obtained on the TGA curve at about 12%. This is due to the evaporation of moisture and trapped solvent in the fibers. Stage 2 is from 150°C to 360°C, a weight loss step obtained on the TGA curve at about 19.2%. This is due to the partial decomposition of the PVP side chains and inorganic salts in the precursor fibers. Stage 3 is from 360°C to 600°C, a large weight loss step obtained on the TGA curve at about 48.4%. This is mainly due to the total decomposition of the PVP backbone and inorganic salts. Stage 4 is from 600°C
to 800°C, there is almost no weight loss on the TGA curve, indicating that the thermal decomposition process of the precursor fibers is completed and the pure wurtzite-type structure is formed finally.

Figure 1. TGA curves of as-spun Zn\(_{0.96}\)Co\(_{0.04}\)O/PVP precursor fibers.

Figure 2. XRD patterns of Zn\(_{1-x}\)Co\(_x\)O nanofibers.

The XRD pattern of Zn\(_{1-x}\)Co\(_x\)O (x=0~0.08) nanofibers calcined at 600°C for 2h are shown in Figure 2. The strong and sharp diffraction peaks of (100), (002), (101), (102), (110) and (103) were observed in the five curves, indicating that the doped ZnO is still a hexagonal wurtzite structure. In addition, the doped samples also showed characteristic diffraction peaks of ZnO, and no other
heterogeneous peaks, indicating that Co$^{2+}$ ions have been doped into the lattice of ZnO. The grain size and unit cell parameters of each sample calculated from the XRD data are shown in Table 1. It can be seen from the table that with the increase of Co$^{2+}$ ion content, the lattice constant of the sample increases gradually, while the grain size decreases correspondingly. Because of the ionic radius of Zn$^{2+}$(0.074nm)$>\text{Co}^{2+}$(0.065nm), so Co$^{2+}$ is much easier to occupy Zn$^{2+}$ position in ZnO crystal lattice. Therefore, the grain size is decrease and the lattice constant is increased.

Table 1. The lattice constant and grain size of the sample.

| Sample | Lattice constant /10^{-10} m | Grain size / nm |
|--------|------------------------------|-----------------|
| X=0    | 3.25282 5.20661              | 32.53           |
| X=0.02 | 3.25375 5.20745              | 30.95           |
| X=0.04 | 3.25458 5.20762              | 29.72           |
| X=0.06 | 3.25599 5.20874              | 28.49           |
| X=0.08 | 3.25709 5.21179              | 27.18           |

To further characterize the structure of the Zn$_{1-x}$Co$_x$O nanofibers, FT-IR tests were performed on Zn$_{1-x}$Co$_x$O nanofibers calcined at 600°C. As shown in Figure 3, the absorption peaks around 3432 cm$^{-1}$ and 1640 cm$^{-1}$ are respectively the stretching vibration of the O-H bond and the deformation vibration of the adsorbed water molecules, which is mainly related to the adsorption of the sample on the water in the air[15]. The absorption peak at 2360 cm$^{-1}$ is the characteristic peak of CO$_2$, which can be attributed to the stretching vibration of CO$_2$ adsorbed on the surface of the sample[16]. The absorption peaks at 445 cm$^{-1}$, 455 cm$^{-1}$, 458 cm$^{-1}$ and 460 cm$^{-1}$ represent the lattice vibration of Zn-O [17], and the position of the infrared characteristic absorption peak of Zn-O has a small change, which may be Due to the vibration of the Zn-O-Co bond. Furthermore, it is found in the infrared spectrum that it has no other absorption peak in addition to all the above. So this shows that the metal salts and PVP have completely decomposed after calcination at above 60°C, and target Zn$_{1-x}$Co$_x$O is generated.

Figure 3. FT-IR patterns of Zn$_{1-x}$Co$_x$O nanofibers.
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The SEM image of Zn0.96Co0.04O /PVP composite nanofibers in Figure 4 shows that a large amount of precursor nanofibers are obtained. The surface of the fibers is smooth, with no intercross or bond and the average diameter at about 200nm.

Figure 5 show the SEM image of products after calcined at 600°C. It can be seen that the fibers’ diameter becomes smaller after calcined at 600°C. This is because that the PVP and metal salts have decomposed completely and the organic elements burns and volatilizes at 600°C. Furthermore, due to the crystallization of fibers and the formation of the Zn0.96Co0.04O grains contained in the fibers, the surface of fibers changes from being smooth to being rough.

In order to investigate the elemental composition of the composite nanofibers after heat treatment, the samples were analyzed by EDS. The EDS spectrum of Zn0.96Co0.04O composite nanofibers is shown in Figure 6. It can be seen from the figure that only three elements of Co, Zn and O exist in the sample, which indicates that the inorganic salt and PVP are completely decomposed during the heat treatment.

Table 2 shows that Co:Zn $\approx$ 4%, which indicates that high-purity and impurity-free Zn$_{1-x}$Co$_x$O nanofibers were successfully prepared by electrospinning.
3.2 Infrared Emissivity of Samples

The 8–14μm band is an important band of infrared instrument or infrared system. So the infrared emissivity analyzer is used to measure the infrared emissivity of the samples in the 8–14μm band. The curve of the sample’s infrared emissivity at different concentration is shown in Figure 7.

It can be seen from the figure that the infrared emissivity firstly decreases and then increases with the increasing of doped Co concentration. When x=0.04, the infrared emissivity of the sample reaches a minimum value of 0.76. As the Co content increases, the Co$^{2+}$ entering the gap of the ZnO lattice is gradually increased, which will provide more free electrons for the ZnO nanofibers, increase the
conductivity of the fibers, and also enhance the scattering of infrared photons by the sample. The interstitial ions caused by the increase in doping amount can also become the scattering center of infrared photons, which reduces the infrared absorption of the sample and reduces the infrared emissivity. However, the increase of free electron concentration by doping is limited. As the doping concentration increases, although the Co$^{2+}$ content entering the ZnO lattice increases, excessive doping may cause lattice distortion, resulting in an increase in grain boundaries. The absorption of the infrared photon energy by the sample is increased, so the infrared emissivity of the sample is increased.

4. Conclusions
In summary, The Zn$_{1-x}$Co$_x$O/PVP composite nanofibers are prepared by sol-gel method combined with electrospinning technology. The pure wurtzite structure of Zn$_{1-x}$Co$_x$O nanofibers is all formed when the composite nanofibers are calcined at above 600 $^{\circ}$C for 2h. As the doping concentration increases, The infrared emissivity of the sample decreases first and then increases slowly. When x=0.04, the infrared emissivity of the sample reaches a minimum value of 0.76. So Zn$_{1-x}$Co$_x$O nanofibers have a good prospect in the infrared emissivity nanomaterials. However, further investigation and optimization still need to be done for Zn$_{1-x}$Co$_x$O nanofibers.

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