

Fabrication of CuSn Nanofibers Prepared via Electrospinning

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Abstract

The Cu and CuSn/PVP nanofibers were fabricated by electrospinning method by controlling various parameters. The precursor solution was prepared with copper(II) acetate monohydrate ($\text{Cu}(\text{CH}_3\text{COO})_2$) and tin chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$), and polyvinylpyrrolidone (PVP) for adjusting viscosity. The fabricated nanofibers were calcined at 873 K in Ar atmospheric environment for 5 hours to remove the solvent and polymer. The morphology and diameter of nanofibers were measured by optical microscopy (OM) with Motic image plus 2.0 program. The components and chemical environment were investigated with X-ray photoelectron spectroscopy (XPS). From the XPS survey spectra, we confirmed that CuSn/PVP nanofibers were successfully fabricated. The XPS peaks of C 1s and N 1s were remarkably decreased after calcination of the nanofibers at 873 K. It implies that the PVP was completely decomposed after calcination at 873 K.

Keywords: Nanofiber, XPS, Optical Microscopy, Polyvinylpyrrolidone

1. Introduction

Copper (Cu) and tin (Sn) have many advantages such as abundant reservation, low cost, and harmless to the environment in commercial applications. In additions, Cu nanoparticles can prevent infection by bacteria due to its less toxic and good antibacterial efficiency and it is effective in disinfection with excellent persistence of properties^[1-4].

Cu and Cu alloy have attracted tremendous interest due to their high electrical and thermal conductivities. Also Cu alloys have high corrosion resistance, good mechanical workability, and cost-effective. Therefore those are widely used as materials in various fields^[5]. Sn is mainly applied as tin oxide (SnO_2), and SnO_2 is widely used owing to its excellent optical and electrical properties. SnO_2 is well known to n-type semiconductor which has wide band gap and it is used in fields such as lithium batteries, solar cells, gas sensors, and electromagnetic materials^[6,7].

Electrospinning method, as the most common and large-scale production method for making nanofibers, have the

advantages of low cost, relatively simple to manufacture, and obtains continuous nanofibers having a diameter of several nanometers. The chemical components and diameter of nanofiber were easily controlled by chemical and physical properties of precursor solution^[8-14].

The fabricated nanofibers can be characterized using a variety of analytical instruments. The qualitative or semi-quantitative analysis of consisting elements can be characterized by X-ray photoelectron spectroscopy (XPS) and the structural features of fiber can be analyzed by optical microscopy (OM).

In this study, We fabricated the Cu and CuSn /PVP nanofibers via electrospinning by controlling the viscosity of the precursor solution, feeding rate, and voltage between the precursor solution and a collector. Then the fabricated nanofibers were analyzed the morphological features using OM and confirmed that the fabricated nanofiber showed the desired atomic ratio using XPS.

2. Experimental

CuSn nanofibers were fabricated by electrospinning method using precursor solution. As shown in Fig. 1, the electrospinning setup consists of three major components: a syringe pump, a high voltage power supply, and a drum collector. First, the precursor solution is prepared as follows. 3 mmol copper(II) acetate ($\text{Cu}(\text{CH}_3\text{COO})_2$), 3 mmol tin chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) and various amounts of poly-

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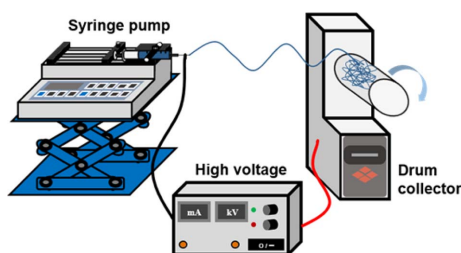


Fig. 1. The schematic diagram of electrospinning system.

vinylpyrrolidone (PVP) were dissolved in 10 mL of 2-methoxyethanol (EGME) and 1 mL of ethanolamine (EAM) under vigorous stirring at room temperature. After the solution was stabilized at room temperature for 12 hours, the precursor solution was loaded into a 10 mL syringe with a 21-gauge needle. For electrospinning, the distance between the needle tip and the collector was kept at 16 cm and the collector surface was covered with aluminum foil. When various high voltages are supplied to the needle tip of the syringe, the CuSn/PVP nanofibers can be obtained. Cu nanofibers were fabricated using copper(II) acetate applying the same method, and the total amount of the solute in the precursor solution was fixed at 6 mmol.

After electrospinning, the as-spun nanofibers were calcined at 600°C in Ar atmosphere to remove the solvent and decompose the polymer from nanofibers, except for the material we want. The heat-treated nanofibers were analyzed using XPS (ESCALab MKII, VG, UK) with Mg K α X-ray source (1253.6 eV) to verify the components and chemical states of the Cu and Sn in the nanofibers. The morphological changes of nanofibers according to various parameter were observed using OM (Motic image plus 2.0 program).

3. Results and Discussion

Among various parameters that can affect the formation of nanofibers, we examined the variation of the fiber morphology as a function of viscosity of the precursor solution, feeding rate, and applied high voltage.

To confirm the effect of feeding rate on the change of nanofiber, all other electrospinning parameters were kept constant. Fig. 2 shows the OM images of the Cu nanofiber according to the feeding rate under a constant condition, with a viscosity of 484 cP and a voltage of 18.6 kV. In general, it can be observed that the beads

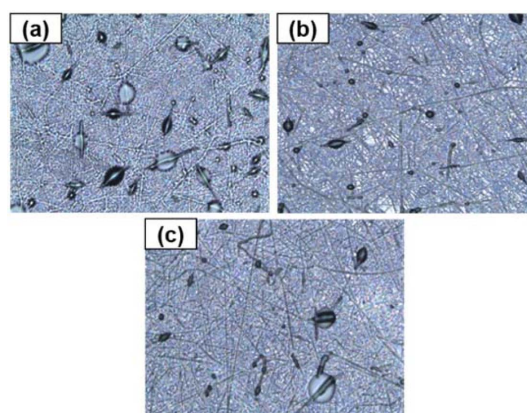


Fig. 2. OM images of Cu nanofibers (10- fold magnification) for different feeding rate at 484 cP and 18.6 kV; (a) 13 μ L/min, (b) 15 μ L/min, and (c) 16 μ L/min.

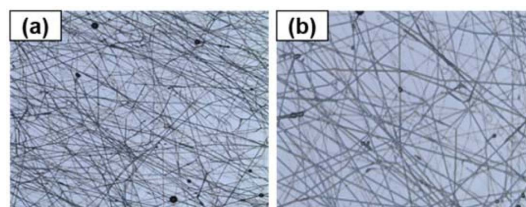


Fig. 3. OM images of CuSn nanofibers (10- fold magnification) for different feeding rate at 575 cP and 18.6 kV; (a) 13 μ L/min and (b) 14 μ L/min.

and the form of not connected nanofibers were appeared. However, the amount of beads was significantly reduced and more continuous nanofibers can be identified when the feeding rate increased from 13 μ L/min to 16 μ L/min, thus structurally stable nanofibers are formed.

Fig. 3 shows the pronounced change of the morphology of the nanofibers which was confirmed with the OM images. It can be seen that the fiber was smoother and the relative amount of beads was decreased when the feeding rate is faster. Therefore, as the feeding rate increases, morphologically improved as uniform nanofibers were formed. This is because as the feeding rate applied to the solution increases, the fluidity and stability increases, then the nanofibers are tangled with each other or are distributed uniformly in a stable form rather than being bundled with beads.

From the results of OM as shown in Fig. 4, the formation of fiber was observed at all voltages, but it can be confirmed that as the voltage applied to the solution becomes larger, only the fiber of uniform shape was

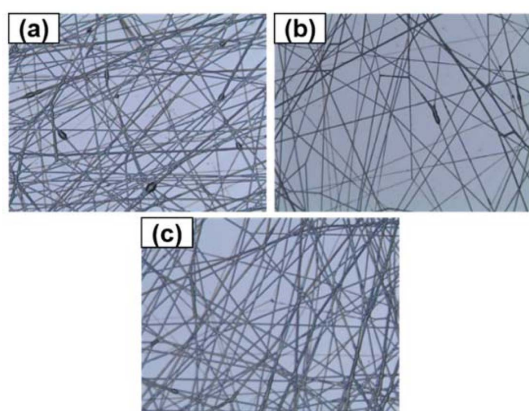


Fig. 4. OM images of CuSn nanofibers (20-fold magnification) for different voltages at 531 cP and 14 $\mu\text{L}/\text{min}$; (a) 19.6 kV, (b) 20.6 kV, and (c) 21.6 kV.

formed without beads. For the solution to be ejected from the needle tip, the force of the electric field must be large enough to overcome the surface tension^[15]. Therefore, if there is not enough voltage to overcome the surface tension, the beads are observed as shown in Fig. 4(a) because the solution forms a discontinuous droplet. Thus, it could imply that as the applied voltage is increased, the stability of solution is improved and a continuous nanofiber can be produced. As a results, we investigated the influence of various parameters such as viscosity, feeding rate, and voltage on precursor solution on the formation of nanofibers. As the parameters of electrospinning increased, the formation of beads in the fiber was relatively decreased, and the surface was smooth and morphologically stable.

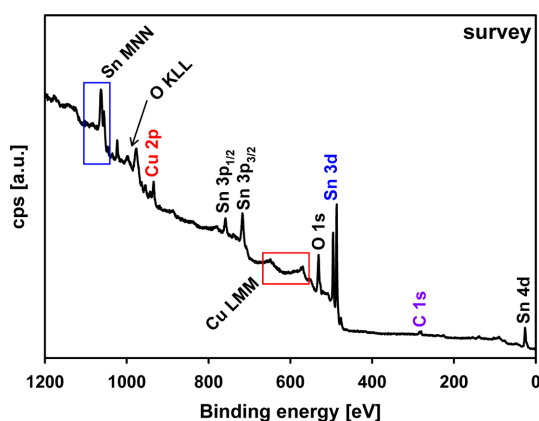


Fig. 5. The survey XPS spectra of CuSn nanofibers.

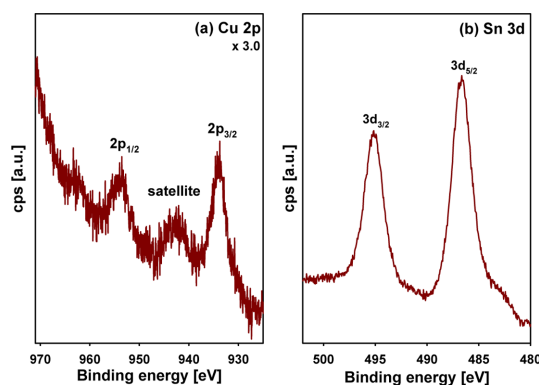


Fig. 6. The XPS narrow spectra of (a) Cu 2p and (b) Sn 3d.

Fig. 5 shows the XPS survey spectra of CuSn nanofiber calcined at 873K. The main peak of Cu and Sn were observed at 934 and 490 eV, respectively. This implies that the CuSn nanofibers were successfully fabricated with intended components. Also another XPS peaks corresponded to O 1s and C 1s were also observed. It is mainly due to the air adsorption of gas particles such as H_2O and CO_2 in the air to the nanofiber. As expected, no peaks corresponding to N 1s, the constituent element of PVP, appeared indicating that PVP was completely decomposed at 600 $^\circ\text{C}$. In addition, three broad peaks assigned to Auger peaks such as Sn MNN, O KLL, and Cu LMM were evolved in CuSn nanofibers as shown in Fig. 5. The two periodic elements O showed KLL peaks in which the electrons of the L shell were transferred to the K shell and then the electrons of the L shell were released due to the energy difference of the transition from L to K shell. Similarly, the Sn and Cu showed the Sn MNN peak and C LMM, respectively.

The high resolution Cu 2p and Sn 3d XPS spectra were collected and shown in Fig. 6(a) and (b), respectively. These peaks were split into doublet due to the spin-orbit-splitting (SOS).

In other words, SOS indicates that the electrons of the same atomic orbital have different binding energies. Also the binding energy value of Cu 2p and Sn 3d peaks were higher than its metallic state. The satellite peak of Cu 2p in CuSn nanofibers was observed. These results implied that Cu and Sn were oxidized.

4. Conclusion

We fabricated Cu and CuSn/PVP nanofibers by elec-

trospinning method. The obtained nanofibers were morphologically analyzed by using OM with varying viscosities of the precursor solution, feeding rates, and voltages. The higher the viscosity of the solution and feeding rate are, the lower the amount of beads and the more stable and continuous nanofibers formation are. In the case of Cu nanofibers, continuous nanofibers were observed from 15 $\mu\text{L}/\text{min}$, which is a high feeding rate, and it is expected that the nanofibers with a more uniform structure will be formed when feeding rate is increased. As the voltage increase, more stable and smooth nanofibers were formed. This is because that the force which can overcome the surface tension was greater with the voltage was increased. The chemical characteristics of the fabricated nanofibers were analyzed by XPS, we confirmed that CuSn nanofibers were successfully formed, and the nanofiber has the desired compositional ratio.

Acknowledgements

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