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Investigation of fundamental parameters affecting electrospun PVA/CuS composite nanofibres

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Abstract

Purpose – The purpose of this paper is to study the preparation of polyvinyl alcohol (PVA)/CuS composite nanofibres, and the effects of solution and process parameters on the resulting nanofibres.

Design/methodology/approach – A facile method coupling self-assembly and electrospinning technology was used to prepare PVA/CuS nanofibres from PVA/$CuCl_2 \cdot 2H_2O$ solution.

Findings – CuS nanoparticles were well dispersed in the composite nanofibres, the dimension of which was in the range of 4-9 nm. Low amount of salt in electrospinning solutions and high-applied voltage were beneficial for forming smooth and small sized nanofibres. The tip-to-collector distance has not affected the morphology of resulting nanofibres.

Research limitations/implications – The orientation of the composite nanofibres was hardly controlled and the diameter distribution of nanofibres was not uniform enough.

Practical implications – The method combining electrospinning and self-assembly provided an effective strategy for preparing nanoparticles doped composite nanofibres.

Originality/value – The morphology of composite nanofibres was well controlled via adjusting the solution and process parameters, therefore, the fibres obtained will have potential applications as controllable nano-optoelectronic materials.

Keywords Fibre testing, Polymers, Voltage

Paper type Research paper

Introduction

Electrospinning technology represents a relatively simple and versatile method for generating one dimensional (1D) nano- and micro- fibular structures (Reneker and Chun, 1996). In a typical electrospinning process, a polymer solution or melt is loaded into a metal capillary. When a strong electrostatic force is applied to the capillary, the solution is ejected and deposited as a nonwoven fibrous mat on a template serving as the ground for the electric charges. Until now, several kinds of nanofibres from polymer (Katta *et al.*, 2004; Zeng *et al.*, 2005; Seema *et al.*, 2006), inorganic (Li and Xia, 2003; Wu *et al.*, 2006; Zhan *et al.*, 2007) and composite (Peng *et al.*, 2006; Xu *et al.*, 2006; Yan *et al.*, 2007) materials have been prepared by the electrospinning method. Recently, nanoparticles doped hybrid nanofibres via electrospinning have received much attention due to their potential applications. Reported examples include TiO_2, ZnO and CdS/polymer composite nanofibres (Wang *et al.*, 2007a, b; Sui *et al.*, 2007). Several groups have used polyvinyl alcohol (PVA), polyethylene oxide (PEO), and other polymers as templates to load inorganic precursors since the solutions of these polymers have suitable viscosity for electrospinning.

In the present paper, the fabrication process of CuS nanoparticle/PVA (nano-CuS/PVA) composite nanofibres by electrospinning PVA/$CuCl_2 \cdot 2H_2O$ solutions will be reported. CuS is an important semiconductor that presents metallic conductivity, transforms into a superconductor at 1.6 K (Liang and Whangbo, 1993) and exhibits fast-ion conduction at high temperatures (Nair and Nair, 1989). Additionally, it also has potential applications as a thermoelectric cooling material, an optical filter, a solar cell, an optical recording material and a superionic material. In this study, the effects of solution parameters, such as viscosity, surface tension,

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conductivity and CuS concentration, and the process parameters, such as tip-to-collector distance and voltage on the morphology and properties of resulting nanofibres will be also investigated. In the TEM analysis, it is found that the CuS nanoparticles are equally dispersed in the PVA nanofibre matrix, and their diameter distribution is between 4 and 9 nm. The coupling of CuS nanoparticles into nanofibre structures will improve the excellent properties of CuS and extend its applications.

Experimental

Materials

Polyvinyl alcohol, copper chloride ($CuCl_2 \cdot 2H_2O$), hydrochloric acid (HCl), sodium sulfide ($Na_2S \cdot 9H_2O$), holey carbon-coated copper grids and platinum electrode. These chemicals were used without further purification. Redistilled water was used as solvent.

Preparation of electrospun solutions and all kinds of nanofibres

Some quantity (Table I) of $CuCl_2 \cdot 2H_2O$ was mixed with 100.0 g PVA aqueous solution ($D_p = 1,750$, 6 wt.%). All the mixed solutions, which were obtained for electrospinning after that, were conducted with vigorous stirring for 16 h. Every solution was delivered to 5.0 ml syringe with a plastic capillary tip (ID: 0.6 mm). A platinum wire connected to the positive electrode of High Voltage Research ES30P power supply was inserted into it, and a metallic plate wrapped with aluminum foil and holey carbon-coated copper grids was used as the collector. The applied voltage and the tip-to-collector distance were adjustable. The electrospun nanofibres were kept in a H_2S atmosphere at the room temperature for 5 h and then annealed at 333 K for 2 h in vacuum to get CuS/PVA nanofibres. All nanofibres were prepared under 40 percent of humidity at 298 K.

Detector of characterization

The morphology of nanofibres was observed using Field Emission Scanning Electron Microscopy (FE-SEM, Sirion, FEI, USA) operated at an accelerating voltage between 18 and 20 kV. Transmission Electron Microscopy (TEM, Hitachi H-8100, Japan) investigation was performed on holey carbon-coated copper grids, using LaB6 radiation. A conductivity meter, a balance, a digital viscometer and an automated surface tensiometer were used to measure the conductivity, mass, viscosity and surface tension, respectively. All the voltages were provided by a power supply of high voltage (0-150 kV). All the measurements were operated at the room temperature.

Results and discussion

Effects of solution properties on the CuS/PVA nanofibres

The CuS nanoparticles/PVA composite nanofibres were successfully prepared by electrospinning PVA/$CuCl_2 \cdot 2H_2O$ solution, followed by exposure to H_2S atmosphere. To testify the existence of CuS nanoparticles in composite nanofibres, the TEM images of pure PVA nanofibres and the composite CuS/PVA nanofibres were compared, depicted in Figure 1. It can be seen from Figure 1b that the CuS nanoparticles were well dispersed in the composite nanofibres and their dimension was in the range of 4-9 nm. To confirm the effects of solution properties on the resulting nanofibres, the viscosity, surface tension and conductivity of solutions for electrospinning were measured, shown in Figure 2. It is noticed that the viscosity and surface tension of solutions are not obviously changed with the increase of the concentration of $CuCl_2$. It is well known that the concentration of polymer is the main factor affecting the viscosity and surface tension of solutions (Fong *et al.*, 1999). When a solid polymer is dissolved in a solvent, the solution viscosity is proportional to the polymer concentration (Huang *et al.*, 2003). Thus, the same concentration of PVA in every solution sample should be responsible for the invariableness of viscosity and surface tension of solutions. In addition, the conductivity of solution increases sharply with the addition of salt, which may result from the increase of the total number of ions.

Influence of applied voltage on the resulting nanofibres

To investigate the effect of external electric field on the resulting nanofibres, nano-CuS/PVA (PC2) composite nanofibres under different applied voltages are manufactured, and their SEM images are shown in Figure 3. Higher applied voltage favors the formation of thinner nanofibres with more uniform diameter distribution (Figure 3d). This phenomenon may originate from two reasons. First, the stronger the electric field, the larger the net charge density carried by the jet in the electrospinning process. Second, during the traveling of a solution jet from capillary to the collector, the primary jet may be split into multiple jets (Bergshoef and Vancso, 1999; Koombhongse *et al.*, 2001). The higher the applied voltage, the more the number of jets will be. Therefore, the dual effects lead to the generation of thinner and more uniform composite nanofibres.

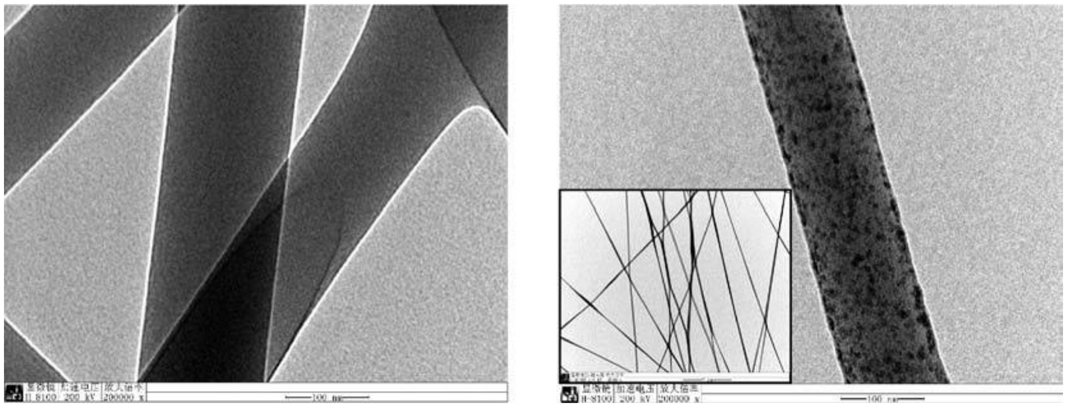
Influence of tip-to-collector distance on the resulting nanofibres

The influence of tip-to-collector distance on the as-prepared nanofibres was also studied. Figure 4 exhibited the SEM images of nano-CuS/PVA (PC2) composite nanofibres obtained under different tip-to-collector distances. With the increase of the tip-to-collector distance, almost no

Table I Compositions of the solutions for electrospinning (unit: g)

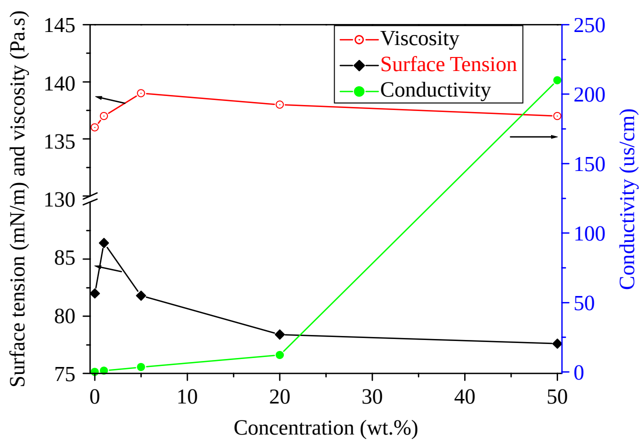
Name	PVA (6 percent)	$CuCl_2 \cdot 2H_2O$	PVA:$CuCl_2$ (wt.%)
PC1	100	0.0000	100:0
PC2	100	0.0761	100:1
PC3	100	0.3806	100:5
PC4	100	1.5224	100:20
PC5	100	3.8061	100:50

Figure 1 The TEM images of PVA/CuS composite nanofibres with different concentration of CuS: (a) PC1; (b) PC3



(a) (b)

Figure 2 Three kinds of curve of all PVA/$CuCl_2$ solutions: (a) the viscosity; (b) the surface tension; (c) the conductivity



conspicuous changes in the morphology of nanofibres were observed. Deitzel thought the increase of tip-to-distance favored the formation of thinner fibres (Deitzel *et al.*, 2001). Increasing the tip-to-collector distance is equal to prolonging the time of elongation of the solution jet in the air. Thus, the dimension of nanofibres should be smaller. But, to some extent, the increase of distance may weaken the electric field force on the jet, which is not beneficial for the decrease of the diameter of nanofibres. It is deduced that the two opposite effects may counteract each other, therefore, no changes are observed in the diameter and morphology of nanofibres.

Influence of CuS concentration on the resulting nanofibres

The SEM images of resultant nano-CuS/PVA composite nanofibres with different CuS concentrations are presented in Figure 5. It can be seen that the nanofibre samples with less CuS (Figure 5a–c) have smooth surface, and the average diameter of nanofibres decreases with increasing the ratio of CuS. When the weight ratio of $CuCl_2$:PVA reaches as highly as 20:100 (Figure 5d), the surface of nanofibres becomes rough and uneven. With their ratio increases continuously, almost no nanofibres are obtained (Figure 5e). Zussman found that the addition of salt led to a higher charge density on the surface of the solution jet during the electrospinning, which brought more electric charges to the jet (Zussman *et al.*, 2002). When the charges carried by the jet increased, higher elongation forces were imposed to the jet under the electrical field, which resulted in thinner fiber diameters and generation of fibres with beads. Therefore, it is concluded that a low amount of salt in solution for electrospinning is beneficial for forming smooth and small sized nanofibres. This provides another strategy for improving the morphology of nanofibres.

Conclusion

The CuS nanoparticles/PVA composite nanofibres were successfully prepared by the electrospinning method, followed by self-assembly. The CuS nanoparticles are well dispersed in the composite nanofibres, and their dimension is in the range of 4-9 nm. With the increase of the concentration of $CuCl_2$ in solutions for electrospinning, the conductivity of solutions increases sharply, whereas the viscosity and surface tension have no obvious changes. A low amount of salt in solutions is beneficial for forming smooth

Figure 3 The SEM images of PVA/CuS (PC3) composite nanofibres obtained at different voltages (under 20 cm): (a) 14 kV; (b) 16 kV; (c) 18 kV; (d) 20 kV

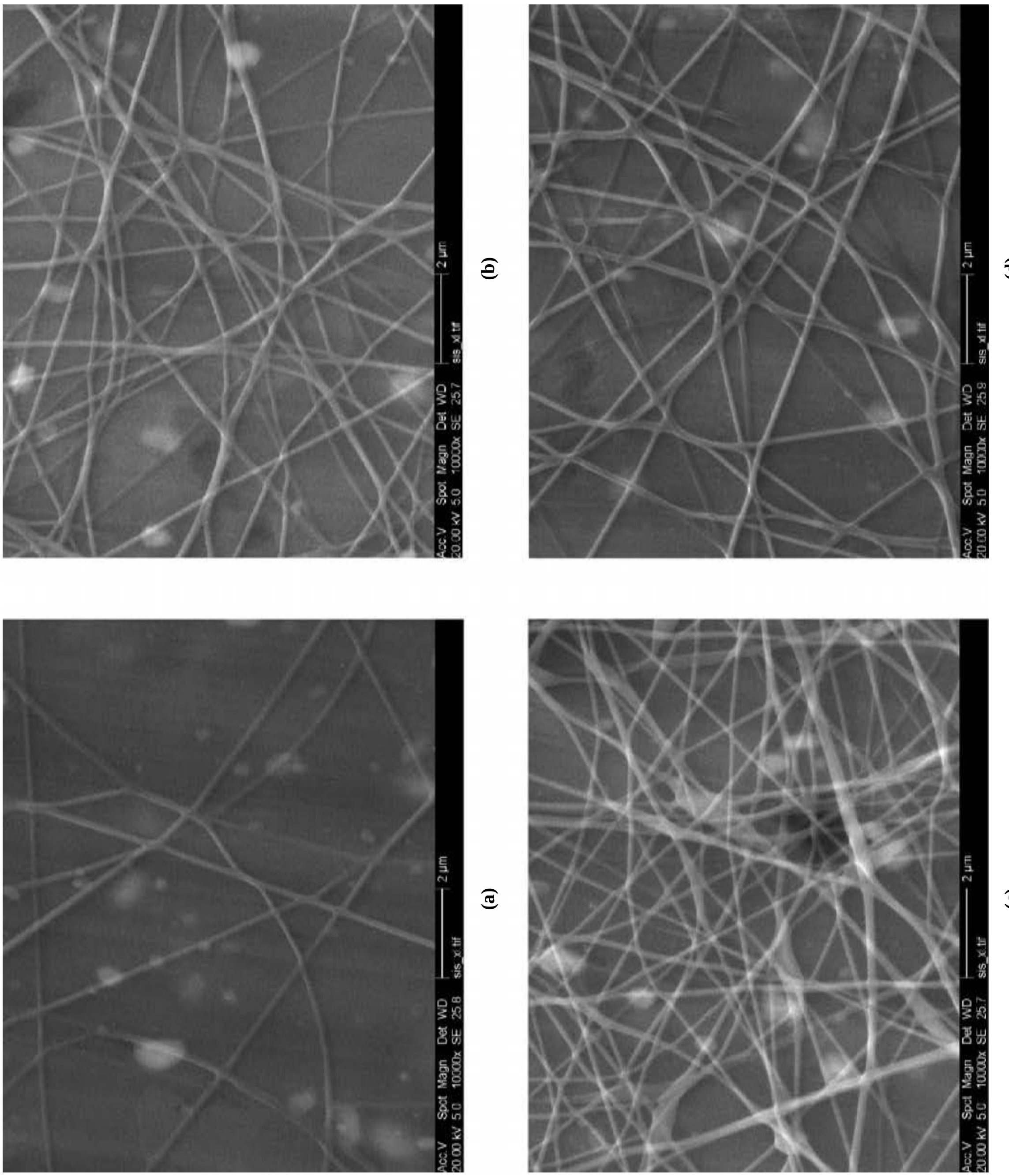


Figure 4 The SEM images of PVA/CuS (PC2) composite nanofibres obtained at different tip-to-collector distances (under 20 kV): (a) 15 cm; (b) 20 cm; (c) 25 cm; (d) 30 cm; (e) 40 cm

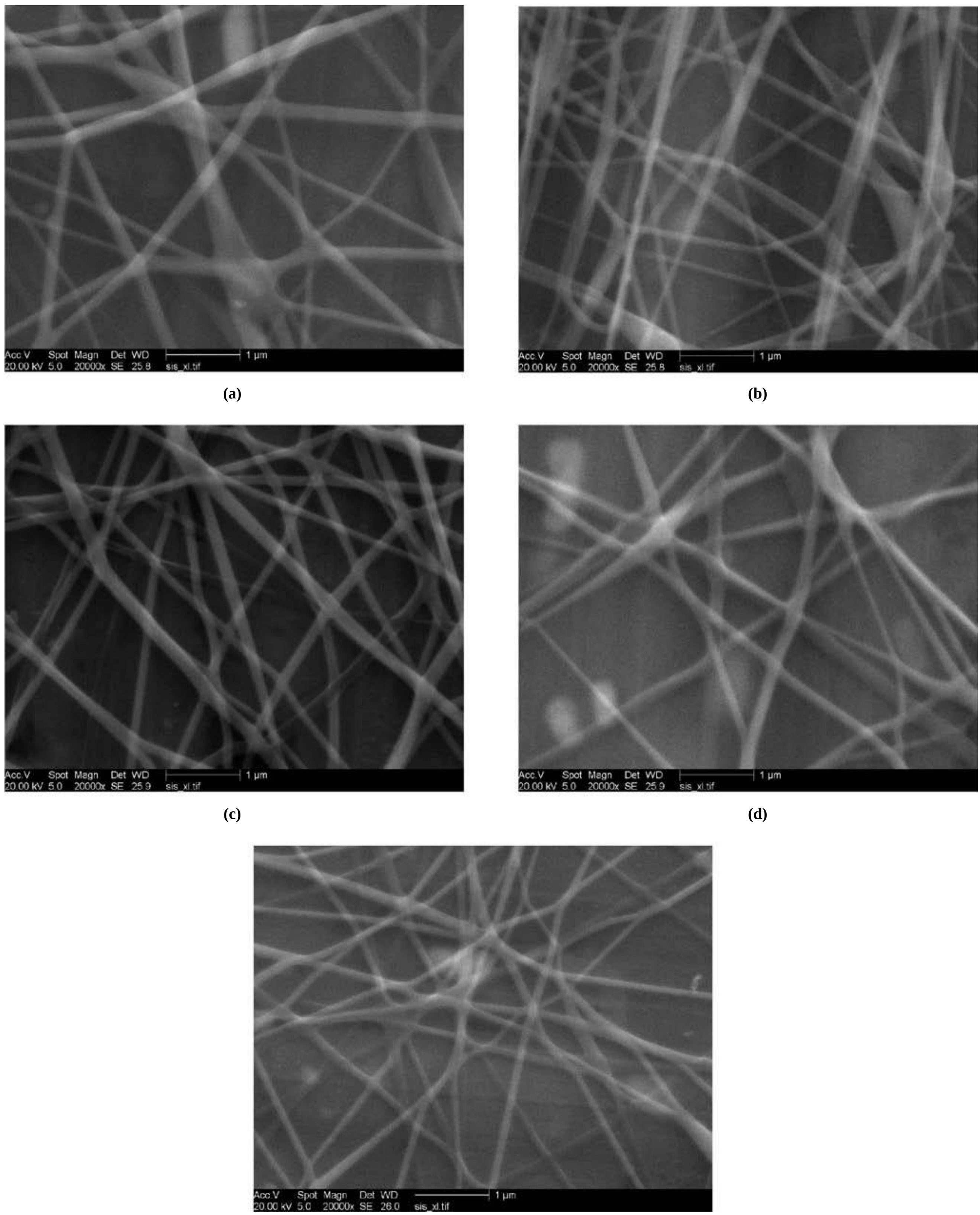
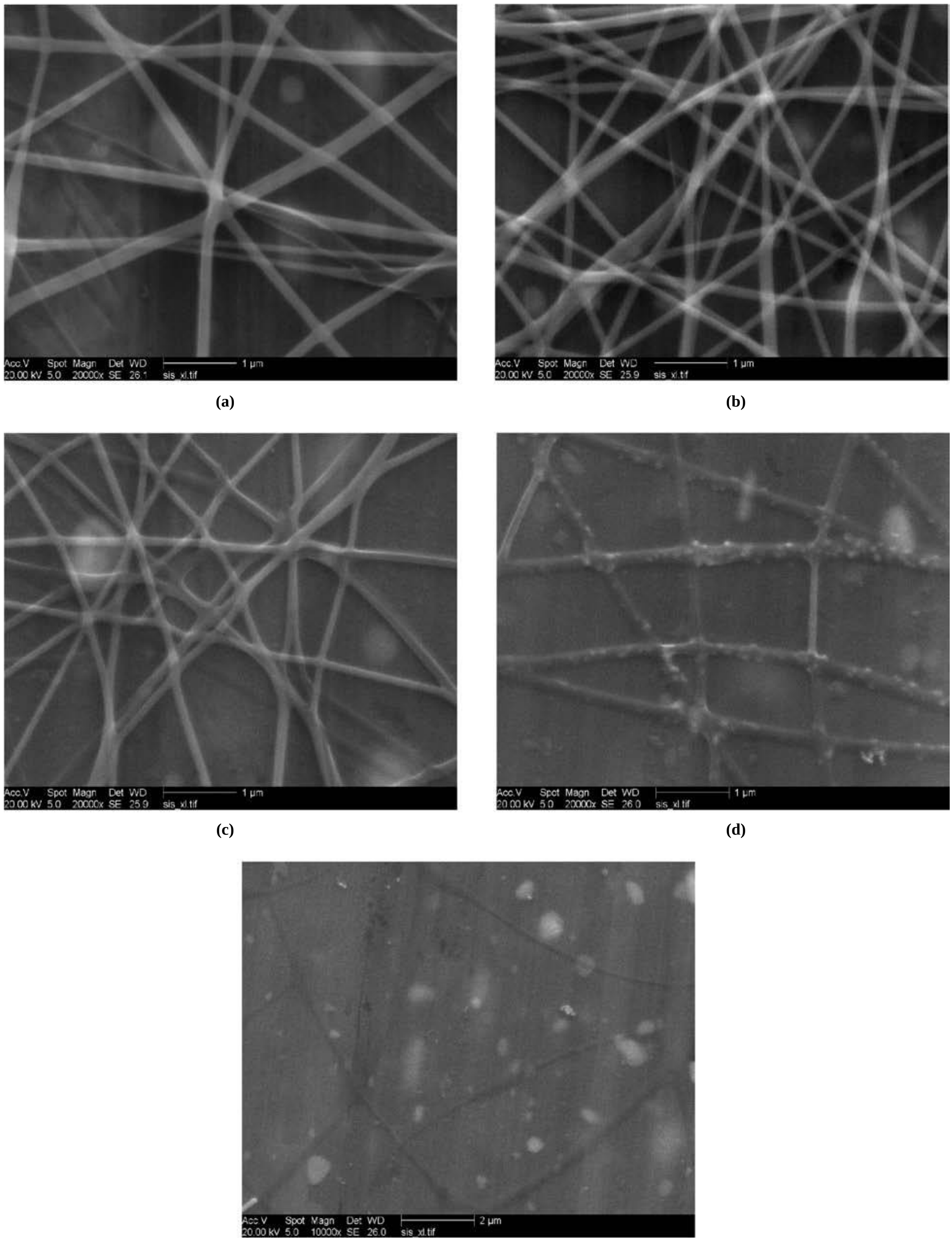


Figure 5 The SEM images of PVA/CuS composite nanofibres with different concentration of CuS (under 20 kV, 25 cm): (a) PC1; (b) PC2; (c) PC3; (d) PC4; (e) PC5



and small sized nanofibres. It is also found that the tip-to-collector distance has not affected the morphology of resulting nanofibres and higher applied voltage favors the formation of thinner nanofibres with more uniform diameter distribution.

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