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Hyung-Seok Lim^a; Bumsu Kim^b; Kyung-Do Suh^a

^a Division of Chemical Engineering, College of Engineering, Hanyang University, Seoul 133-791, Republic of Korea ^b Division of Inorganic Chemistry Exam, Bureau of Chemistry & Biotechnology Exam, Korean Intellectual Property Office (KIPO), Daejeon 302-701, South Korea

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Multiwalled carbon nanotube/SiO₂ composite nanofibres prepared by electrospinning†

Hyung-Seok Lim^a, Bumsu Kim^b and Kyung-Do Suh^{a*}

^aDivision of Chemical Engineering, College of Engineering, Hanyang University, Seoul 133-791, Republic of Korea; ^bDivision of Inorganic Chemistry Exam, Bureau of Chemistry & Biotechnology Exam, Korean Intellectual Property Office (KIPO), Daejeon 302-701, South Korea

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Carbon nanotube (CNT)/SiO₂ composite nanofibres were fabricated by electrospinning treated calcination under nitrogen atmosphere. To obtain CNT/SiO₂ composite nanofibres, functionalised CNTs (fCNTs) were prepared by chemical oxidation and mixed with tetraethyl orthosilicate:H₂O:H₃PO₄:poly(vinyl alcohol) solutions. The resulting solutions were electrospun under adjusted parameters and the properties of the composite nanofibre solution were measured. The dispersity and direction of CNTs in the composite nanofibres were also monitored. By using fCNTs, the CNTs were well dispersed in CNT/SiO₂ composite nanofibres by improving the dispersity of CNTs in the TEOS sol-gel/PVA solution. fCNTs can therefore be used to enhance the dispersity and direction of CNTs in SiO₂ composite nanofibres prepared by electrospinning.

Keywords: ceramic-matrix composites; carbon nanotubes; composite nanofibres

1. Introduction

Nanofibres have been extensively researched because of their unique properties, such as low weight and large surface area to volume ratio. Many potential applications for nanofibres have been proposed, including sensors, nanocomposites, biomaterials, filtration, device wipes, electrical applications and wound dressings [1,2].

Recently, electrospinning has been utilised to efficiently produce continuous nanofibres [3,4]. Specifically, composite nanofibres using carbon nanotubes (CNTs) produced by electrospinning have attracted interest because of the electrical, thermal, mechanical and chemical properties of CNTs [5–8]. Though CNT/polymer composite nanofibres and CNT/TiO₂ nanofibres prepared by electrospinning have been studied by other research groups [9–13], CNT/SiO₂ composite nanofibres have not yet been studied.

Herein, CNT/SiO₂ composite nanofibres were synthesised by electrospinning. To improve the dispersity of CNTs in composite nanofibres, functionalised CNTs (fCNTs) were used. The properties (viscosity, conductivity and dispersity) of TEOS

*Corresponding author. Email: kdsuh@hanyang.ac.kr

†H.-S. Lim and B. Kim contributed equally to this work.

solutions mixed with fCNTs were measured to investigate the effect of fCNTs on electrospinning.

After electrospinning, CNT/SiO₂ composite nanofibres were analysed by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR). In addition, the morphology of CNT/SiO₂ composite nanofibres was compared with SiO₂ nanofibres fabricated under the same experimental conditions. The surface of composite nanofibres was characterised by scanning electron microscopy (SEM). Furthermore, the dispersity of CNTs in composite nanofibres was observed by transmission electron microscopy (TEM).

The fCNTs were observed to be well dispersed in the SiO₂ matrix of the composite nanofibres during electrospinning. In addition, the direction of fCNTs in composite nanofibres was parallel to the direction of spinning flow. Therefore, the properties of CNT/SiO₂ composite nanofibres may be improved by using fCNTs.

2. Experimental

2.1. Materials

Multiwalled CNTs (MCNTs) (greater than 95 wt% purity) were supplied by Iljin nanotech. Tetraethyl orthosilicate (TEOS 98%) and poly(vinyl alcohol) (PVA Mw: 85,000–124,000) were purchased from Sigma Aldrich. Sulphuric acid was purchased from Junsei Chemical Co, Ltd. Nitric acid was purchased from Samchun. Phosphoric acid (H₃PO₄) was purchased from Yakuri.

2.2. Chemical oxidation of CNTs

MCNTs were functionalised by sonication in a mixture of nitric acid and sulphuric acid (3 : 1) for 6 h at room temperature [14]. The solution was diluted with distilled deionised water (DDI), and the mixture was dispersed and separated by a centrifugal separator. This procedure was repeated until no sediment was observed. Finally, functionalised MCNTs (fMCNTs) were diluted to 0.0005 g fMCNTs per 1 g in DDI water.

2.3. Preparation of fMCNT/SiO₂ nanofibres

Initially, the diluted fMCNT solution was mixed with TEOS and H₂O. H₃PO₄ was slowly dropped into the prepared fMCNT/TEOS/H₂O mixtures at room temperature over 5 h (the molar ratio of TEOS/H₂O/H₃PO₄ was 1 : 11 : 0.01) [15]. Finally, the 4 wt% PVA solution was slowly added to the solutions, which were heated in an oil bath for 12 h at 60°C. The obtained mixtures were directly electrospun with an electrospinning device (NanoNC) under fixed conditions (voltage: 20 kV, distance between the tip and collector: 10 cm, jet rate: 1 mL/h). After electrospinning, composite nanofibres were heated in an oven at 50°C for 2 h and were calcinated at 800°C at the rate of 5°C/min under nitrogen atmosphere for 5 h.

2.4. Characterisation

The properties of the fMCNT/TEOS/H₂O/H₃PO₄/PVA mixture for electrospinning were measured with a viscometer (Brookfield, DV-I+), conductometer (LaMotte, Con6) and

dispersity measurement device (Formulation, Turbiscan Lab expert). The fM/CNT/SiO₂ composite nanofibres were characterised by FT-IR (Nicolet, Magna IR-550), XRD (Rigaku, D/MAX 2500), SEM (JEOL, JSM-6300) and TEM (JEOL, JEM-2000EX).

3. Results and discussion

Figure 1 shows electrospun SiO₂ nanofibres with various viscosities and heating time of TEOS/H₂O/H₃PO₄/PVA. The viscosity of the TEOS/H₂O/H₃PO₄/PVA solutions was controlled by changing the concentration of PVA, as given in Table 1. The heating time

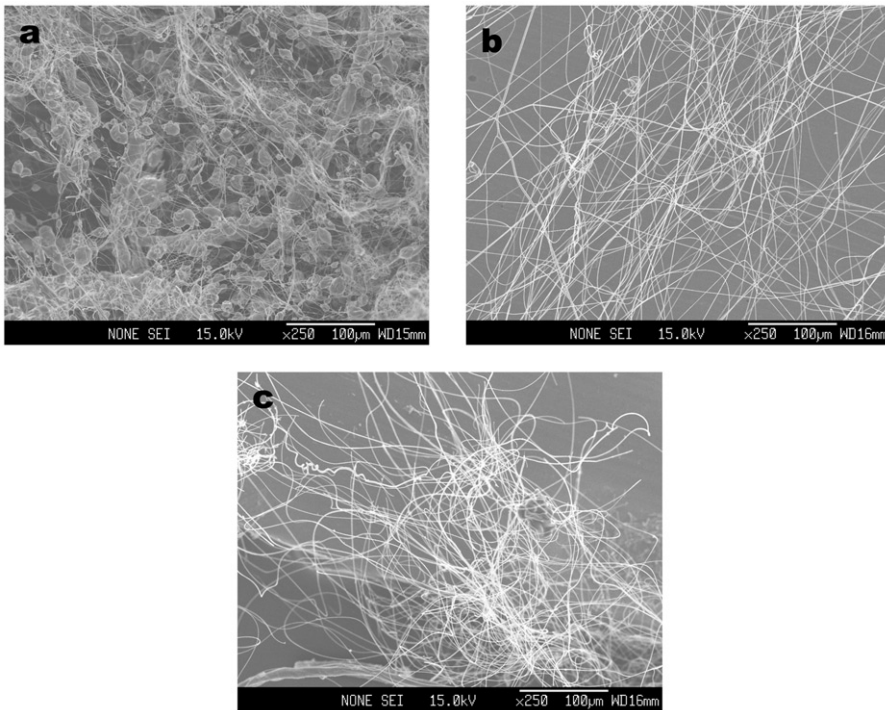


Figure 1. The morphology of SiO₂ nanofibres prepared by electrospinning under different conditions: (a) sample (a) in Table 1, (b) sample (b) in Table 1 and (c) sample (c) in Table 1.

Table 1. The properties of SiO₂ nanofibres prepared by electrospinning under different conditions.

	Sample (a)	Sample (b)	Sample (c)	Sample (d)
Viscosity (cp)	840	1175	1830	4287
Heating time (h)	10	10	12	15
Concentration of PVA solution (wt%)	2	4	4	4
Morphology of nanofibres	Many beads on nanofibres	Some beads on nanofibres	Continuous nanofibres without beads	No nanofibres

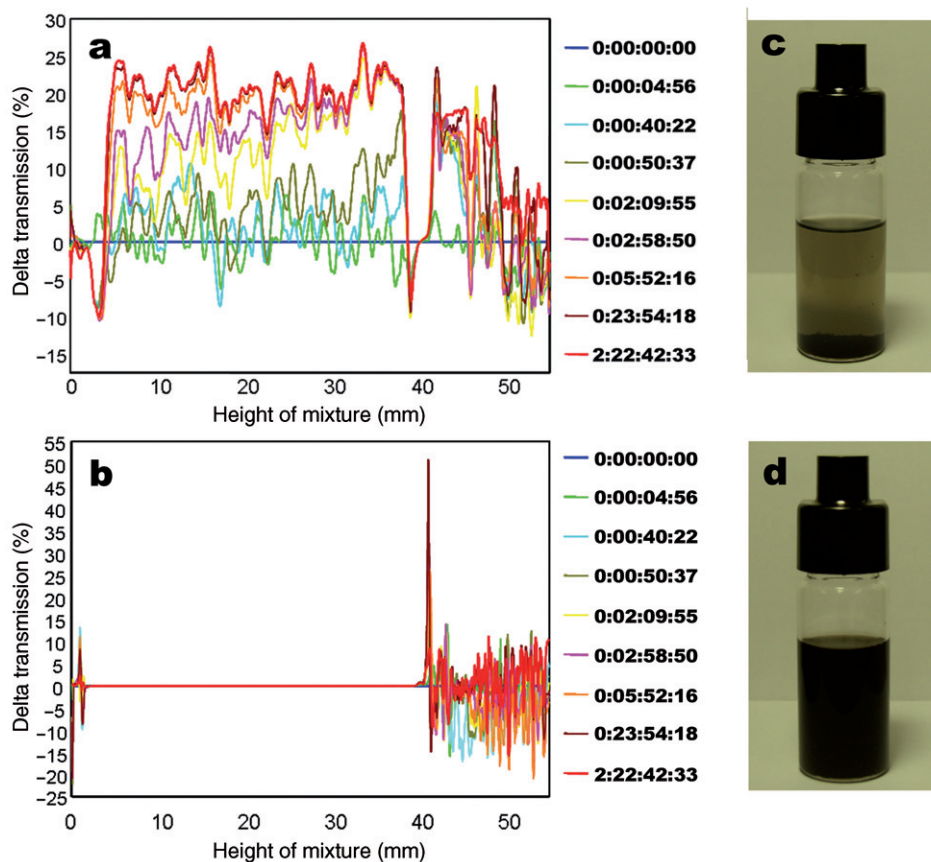


Figure 2. The transmission change of fMCNT/TEOS/H₂O/H₃PO₄/PVA solutions with different sonication times ((a–c) fMCNT/TEOS/H₂O/H₃PO₄/PVA solutions with 1 h sonication and (b and d) fMCNT/TEOS/H₂O/H₃PO₄/PVA solutions with 3 h sonication).

at 60°C varied from 10 to 15 h. The number of beads on the SiO₂ nanofibres decreased with increasing the concentration of PVA from 2 to 4 wt%. The heating time was a crucial parameter to control the number of beads on the SiO₂ nanofibres because the viscosity of the TEOS/H₂O/H₃PO₄/PVA solution was a function of the heating time. Continuous SiO₂ nanofibres (average diameter: 570 nm) without beads were electrospun by adding 4 wt% PVA and heating TEOS/H₂O/H₃PO₄/PVA solutions at 60°C for 12 h. This condition was used to fabricate fMCNT/SiO₂ composite nanofibres.

Before electrospinning, the dispersity of fMCNTs in the TEOS/H₂O/H₃PO₄/PVA solutions was investigated, as shown in Figure 2. The sonication time was observed to be a crucial factor for the dispersity of fMCNTs. After sonicating fMCNT solutions for 1 h, the transmission of solutions increased with time because the fMCNTs precipitated slowly, as shown in Figure 2(a). Most fMCNTs precipitated after 24 h, as shown in Figure 2(c). However, the transmission of fMCNT solutions was unchanged after 3 days when fMCNT solutions were sonicated for more than 3 h, as shown in Figure 2(b). No sediment was observed after 3 days, as shown in Figure 2(d). fMCNTs were not dispersed in

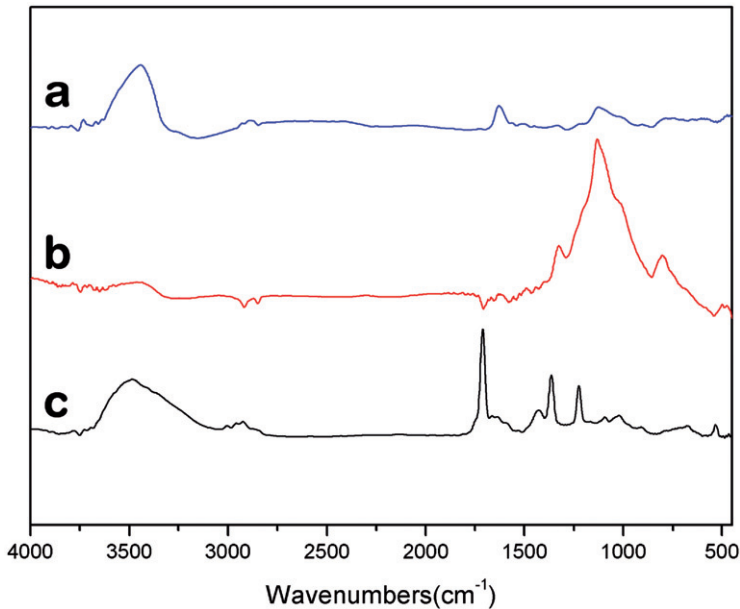


Figure 3. FT-IR spectra of SiO₂ nanofibres and fMCNT/SiO₂ composite nanofibres (a: SiO₂ nanofibres, b: SiO₂ nanofibres after calcinations at 800°C under nitrogen atmosphere, c: fMCNT/SiO₂ composite nanofibres).

SiO₂ composite nanofibres when the fNCNT/TEOS/H₂O/H₃PO₄/PVA solutions were sonicated for 1 h.

Figure 3(a) shows the FT-IR spectra of SiO₂ nanofibres and fMCNT/SiO₂ composite nanofibres after electrospinning. Without fMCNTs, SiO₂ nanofibres had a broad peak near 3448 cm⁻¹ which was caused by stretching vibrations of the hydroxyl group of Si-OH and PVA solution. Several peaks near 1000 cm⁻¹ were due to the stretching vibration of SiO₄ networks, including Si-O and Si-O-Si. After calcination of SiO₂ nanofibres at 800°C, hydroxyl groups (the broad peak near 3448 cm⁻¹) and organic groups (peaks near 1400–1700 cm⁻¹) disappeared, as shown in Figure 3(b). It was observed that fMCNT/SiO₂ composite nanofibres had a -COOH peak at approximately 1700 cm⁻¹ as the carboxylic acid groups were functionalised on the surface of fMCNTs via chemical oxidation, as shown in Figure 3(c).

Figure 4 shows the XRD patterns of fMCNT/SiO₂ composite nanofibres. After calcination at 800°C, a broad peak appeared near $2\theta = 22^\circ$, corresponding to the plane of amorphous SiO₂ in fMCNT/SiO₂ composite nanofibres.

Figure 5 shows the surface morphology of fMCNT/SiO₂ composite nanofibres imaged with SEM. The rough surfaces of composite nanofibres were observed after calcination at 800°C under nitrogen atmosphere because some fMCNTs protruded from the SiO₂ matrix. SiO₂ nanofibres electrospun under the same condition had smooth surfaces without beads, as shown in Figure 1(c).

The viscosity and conductivity of the TEOS/H₂O/H₃PO₄/PVA solutions changed with incorporated fMCNTs, as given in Table 2. Though the viscosity of the TEOS/H₂O/H₃PO₄/PVA solution decreased with fMCNTs, beads were not observed on the surface of

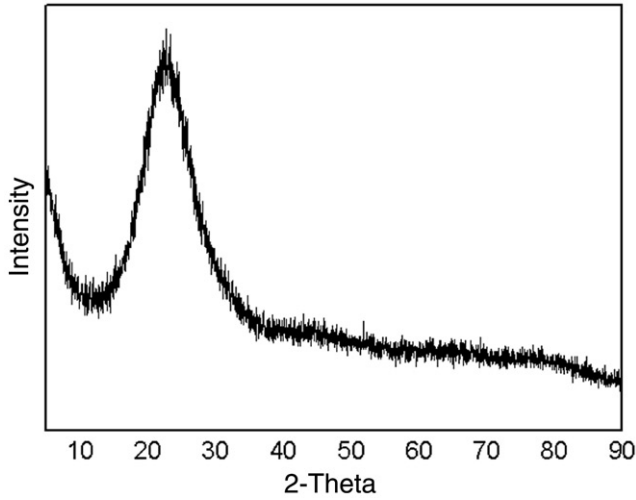


Figure 4. XRD spectrum of fMCNT/SiO₂ composite nanofibres after calcination at 800°C under nitrogen atmosphere.

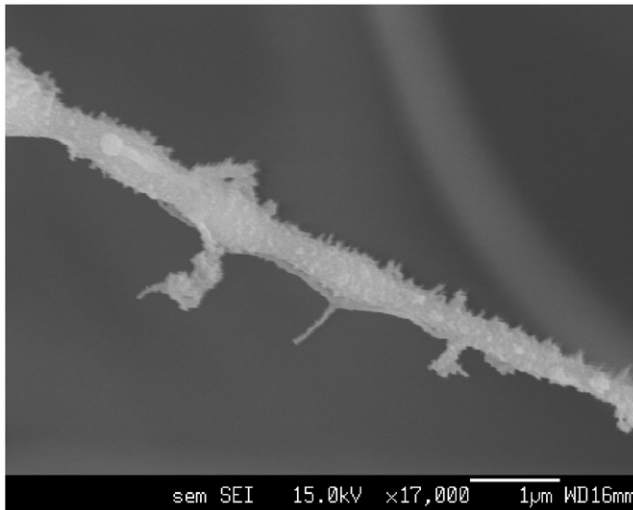


Figure 5. The morphology of fMCNT/SiO₂ composite nanofibres after calcination under nitrogen atmosphere imaged by SEM.

fMCNT/SiO₂ composite nanofibres. In addition, the conductivity of TEOS/H₂O/H₃PO₄/PVA increased with fMCNTs. By changing the viscosity and conductivity of TEOS/H₂O/H₃PO₄/PVA by the addition of fMCNTs, the average diameter of fMCNT/SiO₂ composite nanofibres were 549 nm, which was finer than the diameter of SiO₂ nanofibres without fMCNTs (570 nm).

Figure 6 shows the TEM images of fMCNT/SiO₂ composite nanofibres after calcination. The fMCNTs were not broken because MCNTs have superior thermal

Table 2. The viscosity and conductivity of TEOS/H₂O/H₃PO₄/PVA and fMCNT solution /TEOS/H₂O/H₃PO₄/PVA solutions.

	Viscosity (cp)	Conductivity (mS/cm)
TEOS/H ₂ O/H ₃ PO ₄ /PVA	1830	5.9
fMCNT solution/ TEOS/H ₂ O/H ₃ PO ₄ /PVA	230	7.66

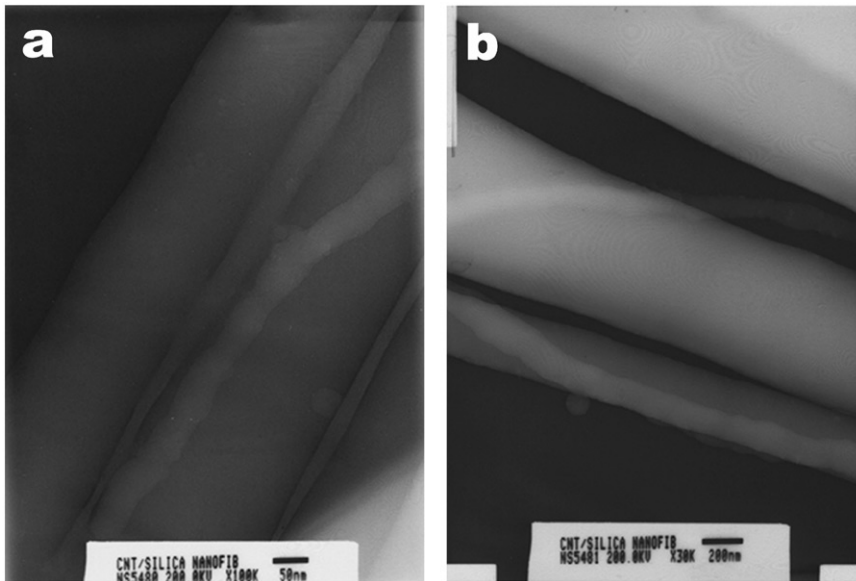


Figure 6. The morphology of fMCNT/SiO₂ composite nanofibres after calcination under nitrogen atmosphere imaged by TEM.

stability under nitrogen atmosphere [16]. Also fMCNTs were well dispersed in the SiO₂ matrix, as shown in Figure 6(a). In addition, the direction of fMCNTs in the SiO₂ matrix was parallel to the direction of electrospinning flow. Furthermore, fMCNTs protruding from the SiO₂ matrix were observed, as shown in Figure 6(b).

4. Conclusion

CNT/SiO₂ composite nanofibres were synthesised by electrospinning treated calcination under nitrogen atmosphere. The fMCNTs were used to improve the dispersity and direction of CNTs in the composite nanofibres. The properties (viscosity, conductivity and dispersity) of the fMCNT/TEOS/H₂O/H₃PO₄/PVA solutions for electrospinning were important factors for controlling the morphology of CNT/composite nanofibres. Therefore, fMCNTs may be used to improve the dispersity and direction of CNTs in SiO₂ composite nanofibres by electrospinning.

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