

Study on TiO₂ Nanoparticles Distribution in Electrospun Polysulfone/TiO₂ Composite Nanofiber

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ABSTRACT: Composite nanofibers composed of organic polymer and inorganic nanomaterials have huge potential to be used in different industrial applications. However, the main concern on the use of composite nanofibers is the distribution properties of nanomaterials in the polymeric matrix. The effect of the capillary tip charge on the additive distribution in the electrospun nanofiber has been previously studied and can be found in the literature. In this study, focus is placed on the investigation of TiO₂ nanoparticles (TiO₂ NPs) distribution in the polysulfone (PSF) nanofiber. X-ray Photoelectron Spectroscopy (XPS) was conducted to measure the percentage of TiO₂ on the surface of the prepared PSF/TiO₂ composite nanofiber. The results showed that there was no TiO₂ NPs on the surface of the nanofiber for up to 10 nm in depth. TiO₂ nanoparticles were mainly found in the center of the nanofiber due to the accumulation of the hydrophobic PSF at the surface of the composite nanofiber. The findings of this work can provide better interpretation of the impact of the interfacial tension on the distribution of the inorganic nanomaterials in the electrospun nanofiber.

KEYWORDS: Electrospinning; Nanofiber; Polysulfone; TiO₂; Interfacial tension; Radial distribution.

INTRODUCTION

Nanoparticles have been embedded in composite nanofiber for various reasons such as to improve mechanical

property of nanofiber or to introduce electrochemical property, etc. [1, 2]. Based on the needed application

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the nanoparticles need to be concentrate in the center, or at the surface of the nanofiber, or homogeneously distribute in the polymer matrix of the nanofiber [3]. This phenomenon is very important for drug-loaded nanofiber synthesis. It is because the presence of nanoparticles will directly affect the drug release rate. However, due to the insufficient research on this area, assumption on the particle distribution is always made based on drug releasing model [4].

There are several parameters that can affect the distribution of the embedded nanoparticles in the composite nanofiber. Several works have been conducted to investigate the effect of the electric charge on the distribution of the component in the electrospun nanofiber [3, 5, 6]. It was found that upon incorporation of electrostatic charged nanoparticles, the developed nanofiber could absorb or repulse the electronegative atoms [5], charged group of the molecules [6] and ions [3] in the polymer solution.

Another parameter that can affect the nanoparticle distribution is the system's interfacial tension. Thermodynamic incompatibility between polymers and nanoparticles usually causes demixing of polymer solution. If the polymer solution is exposed to the air, the lowest surface energy components (hydrophobic components) will concentrate at the air interface and as a consequence reduce the system's interfacial tension [7].

In this work, for the first time we will study the effect of the system's interfacial tension on the radial distribution of the titanium dioxide nanoparticles (TiO_2 NPs) in the electrospun nanofiber made of dope solution containing organic polysulfone (PSF) and inorganic TiO_2 NPs. X-ray Photoelectron Spectroscopy (XPS) and Energy-Dispersive X-ray (EDX) spectroscopy studies were carried out to evaluate the presence of the TiO_2 NPs on the surface and bulk of the nanofiber, respectively.

EXPERIMENTAL SECTION

Polysulfone Udel P-1700 (Solvay Advanced Polymers) and TiO_2 NPs with particle size of <21 nm (Degussa P25, Evonik) were used as the main component and additive in the process of composite nanofiber making. N,N-dimethylformamide (DMF, Sigma-Aldrich, 99.8%) was used as the solvent to dissolve PSF pellets.

One gram TiO_2 was first added to 81 gram DMF, followed by 3-h ultrasonication. 18 gram PSF was

then added to the mixture and was continuously stirred at room temperature for 24 h to achieve complete dissolution of the polymer. The prepared solution was then sonicated to remove the air bubbles that might be trapped within the solution. The prepared solution was transferred into a 10 mL plastic syringe, with 9 G blunt-end capillary tip. The electrospinning was conducted using a commercial electrospinning machine (NaBond, China). The distance between the capillary tip and aluminum collector was set at 15 cm. Positive high voltage of 20 kV (DC) was applied to the capillary tip. The solution was spun at a feeding rate of 0.8 mL/h using infusion pump (Veryark TCV-IV, China). The spinning was conducted at 22°C with the relative humidity of 60%.

Nanoscale morphology of the functionalised surface was probed using a Field Emission Scanning Electron Microscope (FESEM SUPRA 35VP ZEISS). The mean diameter of the nanofiber was calculated by measuring the diameter of 50 units of nanofibers using image analysis software (Image J, National Institutes of Health, USA). Chemical composition of the composite nanofiber was analysed using XRD diffractions (D5000 Diffractometer Siemens) with a Cu X-ray tube. The diffractometer was operated at 40 kV and 30 mA. Data were collected for 2 θ from 10° to 90° with a step size of 0.05°. Owing to the small diameter of the electrospun nanofiber and high penetration depth of the EDX analysis [8], it is not possible to examine the radial distribution of the TiO_2 NPs on the nanofiber surface. Therefore, X-Ray Photoelectron Spectroscopy (XPS) (AXIS Ultra DLD, Kratos, U.K.) was used and the results were compared with bulk elemental analysis via EDX [6, 9]. The XPS analysis was done for 6 samples and the scan area for each sample was 700 $\mu\text{m} \times 300 \mu\text{m}$.

RESULTS AND DISCUSSION

Figs. 1 (a) and (b) show the FESEM image of the surface of the nanofiber at two different magnifications. EDX results inserted in Fig. 1 (b) confirmed the presence of the TiO_2 NPs in the nanofiber. Fig. 1 (c) shows the diameter frequency of the PSF/ TiO_2 composite nanofiber with the mean diameter of approximately 540 nm.

The XRD patterns of TiO_2 NPs and PSF-based nanofiber with and without TiO_2 NPs are shown in Fig. 2. The existence of three main peaks at 2θ of 26.1°, 37.1° and 47.9° indicated the properties of TiO_2 NPs and

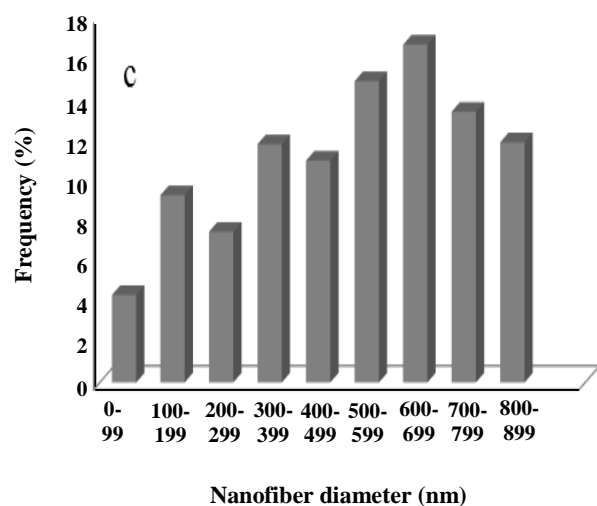
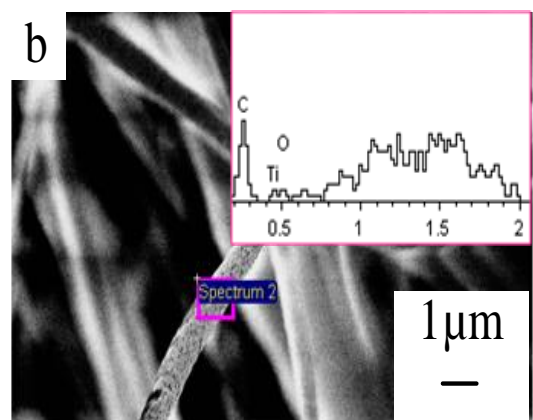
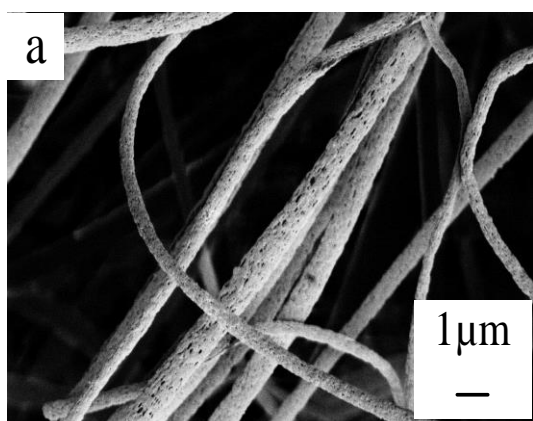


Fig. 1: FESEM images of the nanofiber with (a) 1,000 × and (b) 5,000 × magnification (with EDX results inserted) and (c) nanofiber diameter frequency.

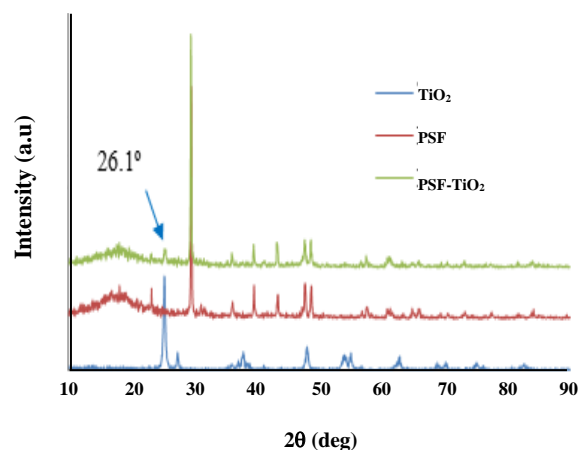


Fig. 2: XRD spectra of TiO₂ NPs, PSF nanofiber (control) and PSF/TiO₂ composite nanofiber.

the results was consistent with the work of Yang & Wang [9]. By comparing the spectra of composite nanofibers with the control sample (i.e. nanofiber without TiO₂ incorporation), it is found that the additional peak of 26.1° that appeared only in PSF/TiO₂ composite nanofiber is a good indication of the successful embedment of TiO₂ NPs in the PSF nanofiber mat.

Fig. 3 presents the XPS spectra of the surface of PSF/TiO₂ composite nanofiber. The peaks with the Binding Energy (BE) of 283, 531, and 167 eV are corresponded to Carbon (C), Oxygen (O) and Sulfur (S) element of polymer structure itself, respectively. However, no peak of the titanium (Ti) was detected at binding energy of 469 eV. Table 1 presents the measured atomic percentages of the surface of PSF/TiO₂ composite nanofiber via XPS.

Based on the EDX and XRD results, we could confirm that TiO₂ NPs do exist in the bulk of fabricated composite nanofiber. But, according to the XPS results, no TiO₂ NPs were found on the surface of the composite nanofiber sample. The main difference of the XPS compared to the EDX and XRD analyses is its high surface sensitivity with analysis depths of about 10 nm. Generally, TiO₂ shows positive charge at the pH < 6 and negative charge at pH > 6 with Iso-Electric Point (IEP) at the pH around 6 [10, 11]. As the pH of the electrospinning dope solution was at around 6.3, it is believed that TiO₂ NPs carry no charge in this condition. PSF on the other hand is known to have no charge, thus

Table 1: Measured atomic concentration of the elements of the surface of PSF/TiO₂ composite nanofiber.

^a Peak	Position BE (eV)	^b FWHM (eV)	Atomic Conc. (%)
C 1s	283.000	3.148	85.40
O 1s	531.000	3.549	11.92
S 2p	167.000	3.241	2.68
Ti 2p	469.000	0.000	Not detected

a) The test was repeated for six times and the presented data in the table is the average of results.

b) FWHM stands for full width at half maximum

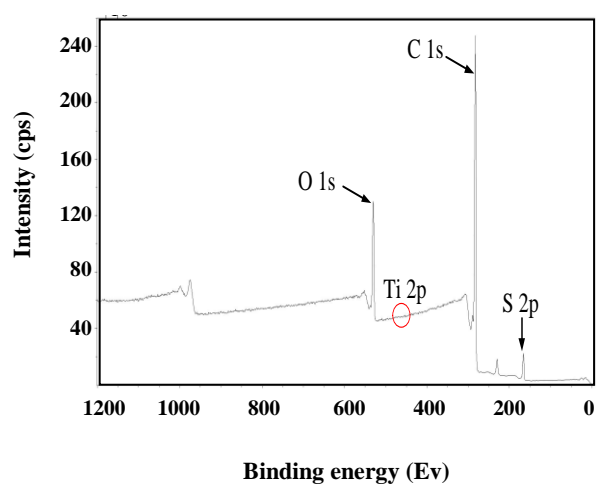


Fig. 3: Wide range XPS spectra of PSF/TiO₂ composite nanofiber.

the effect of electrostatic charge is ruled out as the factor causing the accumulation of PSF at the surface of the nanofiber.

The reason of accumulation of TiO₂ NPs in the center of the nanofiber can be explained by the effect of system's interfacial tension on components distribution. To reduce the system's interfacial tension, hydrophobic components e.g. PSF [12] would concentrate at the air interface surface while hydrophilic TiO₂ NPs would [13] accumulate at the center of the nanofiber [7, 13]. Fig. 4 schematically shows the mechanism of hydrophobic PSF moving to the outer surface of nanofiber while hydrophilic NPs accumulating at the fiber center.

CONCLUSIONS

The elemental study of the PSF/TiO₂ composite nanofiber revealed that the TiO₂ NPs tended to

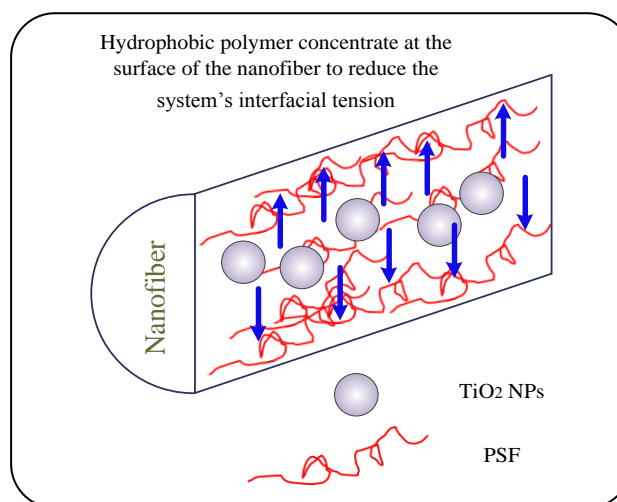


Fig. 4: Schematic of the tendency of hydrophobic PSF moving to the surface of the nanofiber in PSF/TiO₂ composite nanofiber..

accumulate at the center of the nanofiber. The presence of the TiO₂ NPs in the PSF/TiO₂ composite nanofiber was confirmed by XRD and EDX results while XPS results showed that there was no TiO₂ NPs detected at the surface of the nanofiber for up to 10 nm in depth. This finding is important as it provides better understanding on the mechanism of polymer/inorganic dope solution on the radially distribution of the components in electrospun nanofiber.

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