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Multifunctional ZnO/Nylon 6 nanofiber mats by an electrospinning–electrospraying hybrid process for use in protective applications

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Abstract
ZnO/Nylon 6 nanofiber mats were prepared by an electrospinning–electrospraying hybrid process in which ZnO nanoparticles were dispersed on the surface of Nylon 6 nanofibers without becoming completely embedded. The prepared ZnO/Nylon 6 nanofiber mats were evaluated for their abilities to kill bacteria or inhibit their growth and to catalytically detoxify chemicals. Results showed that these ZnO/Nylon 6 nanofiber mats had excellent antibacterial efficiency (99.99%) against both the Gram-negative *Escherichia coli* and Gram-positive *Bacillus cereus* bacteria. In addition, they exhibited good detoxifying efficiency (95%) against paraoxon, a simulant of highly toxic chemicals. ZnO/Nylon 6 nanofiber mats were also deposited onto nylon/cotton woven fabrics and the nanofiber mats did not significantly affect the moisture vapor transmission rates and air permeability values of the fabrics. Therefore, ZnO/Nylon 6 nanofiber mats prepared by the electrospinning–electrospraying hybrid process are promising material candidates for protective applications.

Keywords: electrospinning, electrospraying, Nylon 6, zinc oxide, antibacterial, detoxification

1. Introduction

Electrospun nanofiber mats are characterized by small fiber diameters, controllable pore sizes and high porosities [1]. These properties could be used in protective clothing materials to efficiently adsorb submicron aerosols such as pathogens and toxic chemicals. By introducing functional materials into nanofibers, it is also possible to provide electrospun nanofibers with antibacterial and detoxifying properties.

Extensive research on zinc oxide (ZnO) reveals a gamut of functionalities such as antifungal properties [2], photocatalysis [3] and UV light absorption [4]. Sawai *et al* [5] reported antibacterial properties of ZnO particles against *Escherichia coli* bacteria. Recently, Prasad *et al* [6]

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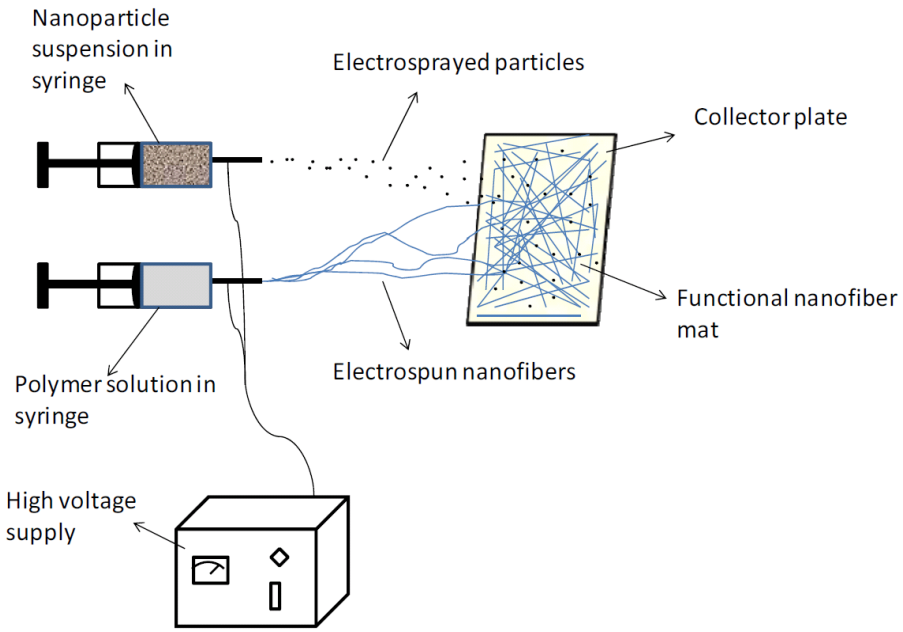

Figure 1. Schematic of the electrospinning–electrospraying hybrid process.

demonstrated that ZnO in the form of nanorods or nanoparticles can detoxify highly toxic chemicals. Therefore, incorporating ZnO into electrospun nanofibers can lead to composite nanofiber mats that have the ability to effectively kill bacteria and detoxify poisonous chemicals. In general, the active particles could be dispersed directly in polymer solution to be electrospun into functional composite nanofibers [7]. However, this process has the limitation of particle aggregation in the polymer solution and related fiber spinning difficulties. In addition, in the resultant composite nanofibers, most nanoparticles are encapsulated in the polymer matrix and thus are not available for providing active antibacterial and detoxifying functions.

This paper presents the preparation of novel ZnO/Nylon 6 nanofiber mats by an electrospinning–electrospraying hybrid process. During that process, Nylon 6 nanofibers were electrospun from a nylon solution, and simultaneously ZnO nanoparticles were electrosprayed using a ZnO suspension. The ZnO nanoparticles in the resultant nanofiber mats are dispersed on the fiber surface and are exposed to the environment; therefore, these functional nanofibers are readily available for active reactions against pathogens and toxic chemicals. This manuscript discusses chemical detoxification and antibacterial activities of functional ZnO/Nylon 6 nanofiber mats. Paraoxon was chosen as a simulant of toxic chemicals [8], and *Bacillus cereus* and *E. coli* were for antibacterial property tests [9].

2. Experimental details

2.1. Materials

Nylon 6 pellets, zinc oxide (ZnO, particle size 50 nm), 2, 2, 2-tri-fluoro ethanol (TFE), methanol, acetone and diethyl **p**-nitro phenyl phosphate (paraoxon) were purchased from Sigma-Aldrich. All reagents were used without further purification.

2.2. Preparation of ZnO/Nylon 6 nanofiber mats

The ZnO/Nylon 6 functional nanofibers were prepared by an electrospinning–electrospraying hybrid process as illustrated in figure 1. Nylon 6 was dissolved in TFE solvent at a concentration of 10 wt%. ZnO nanoparticles (10 wt%) were dispersed in methanol and subjected to ultrasonication for 15 min to obtain a homogeneous ZnO suspension. Nylon 6 polymer solution and ZnO nanoparticle dispersion were loaded into two separate syringes and placed side-by-side on a two-syringe pump. The feed rate was maintained at 1.0 ml h^{-1} for both syringes. The distance between the syringe needle tips and the collector plate was 15 cm. The syringe needles were positively charged with 20 kV using a high-voltage power supply (Gamma ES40P-20W/DAM) to electrospin Nylon 6 nanofibers and simultaneously electrospray ZnO nanoparticles. The prepared ZnO/Nylon 6 nanofiber mats were vacuum dried overnight to remove residual TFE and methanol. For comparison, Nylon 6 nanofibers were also prepared by electrospinning the Nylon 6 solution under similar conditions.

2.3. Characterizations of solution and dispersion properties and nanofiber mat structure

The viscosity of Nylon 6 solution was measured using a rheometer (StressTech HR, Rheologica Instruments AB) at 25 °C with assistance of rheoExplorer V5 software. The ionic conductivities of Nylon 6 solution and ZnO suspension were measured using Orion model 164 conductivity measuring instrument (Orion Research Inc., Boston, MA). The morphology of ZnO/Nylon 6 nanofiber mats was examined

using a JEOL JSM-6400F field emission scanning electron microscope (FESEM) at an accelerated voltage of 5 kV.

2.4. Evaluation of antibacterial activity of ZnO/Nylon 6 nanofiber mats

The antibacterial activity of ZnO/Nylon 6 nanofiber mats was first evaluated qualitatively using the antibacterial activity assessment of textile materials AATCC test method 147-2004. The *E. coli* O157:H7 (FSRU-B387) harboring plasmid pSM433 encoding green fluorescent protein (GFP) was prepared by inoculating 5 mL of Luria–Bertani (LB) broth with a bacterial colony and incubated for 18 h at 37 °C. Using a 4-mm inoculating loop, 5 parallel streaks of bacterial culture were spread across an LB agar plate without refilling the loop between streaks. An aseptically cut, rectangular ZnO/Nylon 6 nanofiber mat specimen was gently pressed transversely face-down across the streak area on the agar plate. Plates were evaluated for clearing and interruption of growth along the streak lines. Since the *E. coli* contained GFP, ultraviolet light (370 nm) was employed to improve visualization. To obtain consistent results, four replicate plates were used for the streak method for each nanofiber mat sample.

For quantitative analysis of the bactericidal effects of the nanofiber mats, we used *E. coli* O157:H7 (B179), a Gram-negative enteric pathogen, and *B. cereus* (B002), a spore-forming Gram-positive pathogen. The pathogens *E. coli* B179 and *B. cereus* B002 were grown in LB agar or broth and tryptic soy agar (TSA), respectively. The bacterial cells were taken from randomly chosen colonies on agar plates and cultured by inoculating into 5 ml LB broth or TSA broth, then incubated for 18 h at 37 °C on a shaker platform at 200 rpm. The independent replications of each culture were prepared. After the incubation period, the cells were harvested by centrifugation (5000 rpm, 10 min, 4 °C, Sorvall RB-5C centrifuge) and resuspended in 5 ml of physiological saline (0.85% NaCl). Cells were diluted to 10^7 CFU (colony forming units) ml^{-1} and used immediately for testing. During testing, the ZnO/Nylon 6 nanofiber mat specimens (5–8 mg) were aseptically prepared and placed in a 1.5 ml micro-centrifuge tube. The saline cell suspension (0.2 ml) containing approximately 10^7 CFU ml^{-1} of the test organism was injected into the tube, completely covering the nanofiber mat. Appropriate positive (cell suspension in saline without nanofiber mat) and negative controls (saline without cells, saline plus nanofiber mat, cells plus a Nylon 6 nanofiber mat), were also included in the experimental design. Samples were incubated for 24 h at 37 °C with gentle agitation at 300 rpm on a shaker platform. After 24 h, cells were enumerated on LB agar (*E. coli*) or TSA (*B. cereus*) plates using a spiral plater (Spiral Biotech Model 4000). After 24 h incubation at 37 °C, bacterial colonies on plates were counted by an automated plate reader (Qcount, Spiral Biotech). The lowest level of detection using this method was approximately 10^2 CFU ml^{-1}. All antibacterial measurements were conducted in a bio-safety Level 2 laboratory in the USDA Agricultural Research Service Laboratory, Department of Food Science, NC State University, Raleigh, North Carolina.

Table 1. Properties of Nylon 6 solution and ZnO suspension.

Measurement	Nylon 6 in TFE (10 wt%)	ZnO in Methanol (10 wt%)
Zero shear viscosity (cP)	110 ± 5	–
Ionic conductivity (μS cm^{-1})	3.7 ± 0.1	175 ± 3

2.5. Evaluation of detoxification properties of ZnO/Nylon 6 nanofiber mats

For detoxification test, a piece of ZnO/Nylon 6 nanofiber mat (∼300 mg) was placed in a glass vial, which was then filled with 8 ml solution of ∼20 μM concentration paraoxon in acetone. For comparison, Nylon 6 nanofiber mat (∼150 mg) and pure ZnO particles (∼150 mg) were also loaded in separate vials and filled with 8 ml of the above-mentioned paraoxon solution. All the vials were stored at room temperature for the detoxifying reaction. After specific time intervals, the solutions were extracted and tested by gas chromatography-mass spectrometry (Agilent 5975B GC-MS, Agilent Technologies, USA) to determine the residual concentration of paraoxon. In the GS-MS spectra, concentration of paraoxon was represented by the area under the peak.

2.6. Air permeability and moisture vapor transmission rate measurements

To evaluate air permeability and moisture vapor transmission rate (MVTR), ZnO/Nylon 6 nanofibers were deposited onto a 50 : 50 nylon/cotton blend fabric by the electrospinning–electrospraying hybrid process. The fabric deposited with pure Nylon 6 electrospun nanofibers and control fabrics without any nanofibers were included in the test. The areal density of ZnO/Nylon 6 and Nylon 6 nanofiber mats were measured by weighing the sample fabric substrate before and after nanofiber deposition at 20 °C and 65% relative humidity.

The air permeability values of ZnO/Nylon 6 and Nylon 6 nanofiber mats deposited on fabric substrate were measured using Frazier air permeability testing instrument. The measurement was carried out according to the ASTM D737-04 standard test method for air permeability of textile fabrics, with a 1.4 mm orifice, 17.7 cm^2 test area, at 762 mm mercury pressure, 20 °C, and 65% relative humidity.

The MVTRs of ZnO/Nylon 6 and Nylon 6 nanofiber mats deposited onto fabric substrate were measured using the ASTM E96-80 standard. Prior to the test, the samples were conditioned at 20 °C and 65% relative humidity for 24 h. The MVTR values were calculated in units of g m^{-2} day^{-1}).

3. Results and discussion

3.1. Preparation and characterization of ZnO/Nylon 6 nanofiber mats

Table 1 shows the viscosity of ZnO suspension and the ionic conductivities of both Nylon 6 solution and ZnO suspension. The measured ionic conductivity and viscosity values

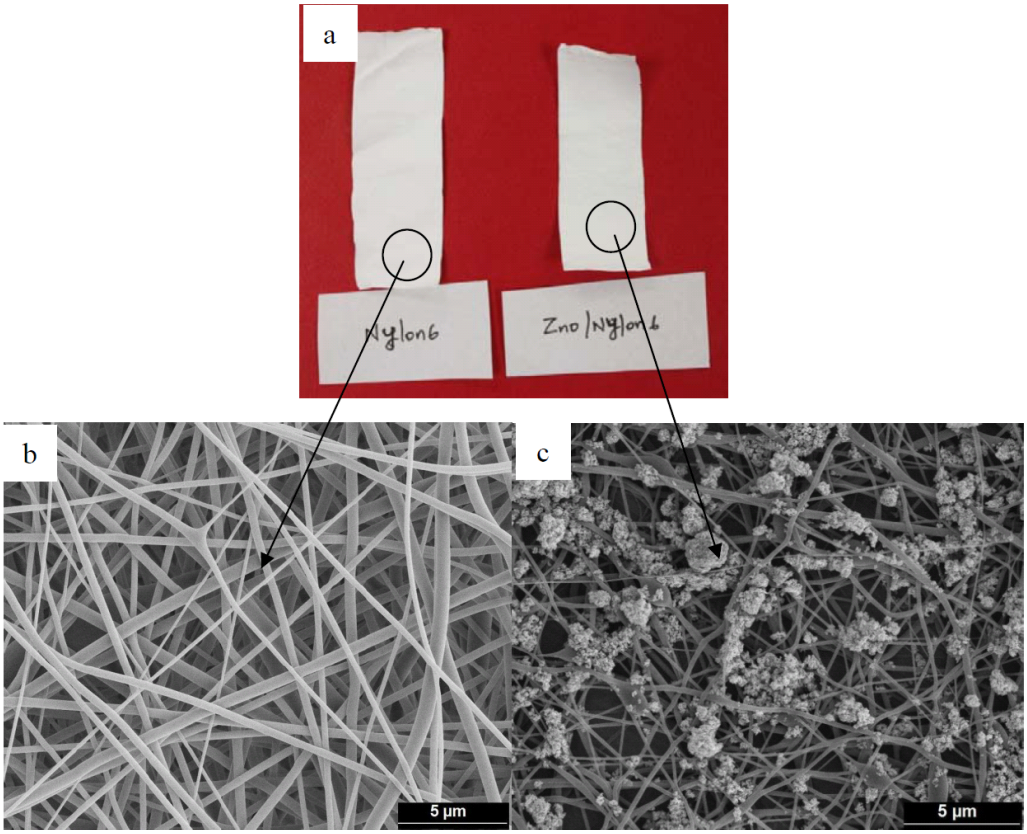

Figure 2. (a) Photographs of Nylon 6 and ZnO/Nylon 6 nanofiber mats, and FESEM image of (b) Nylon 6 and (c) ZnO/Nylon 6 nanofiber mats.

could support a stable electrospinning or electrospraying process [10, 11]. During the hybrid process, the positively charged Nylon 6 solution was ejected and underwent a stretching-and-whipping process resulting in the formation of a long, thin thread. This stretching-and-whipping process is accompanied by the rapid evaporation of the solvent that reduces the jet diameter from hundreds of micrometers to tens of nanometers. The dry fibers are accumulated on the surface of the grounded collector forming a non-woven mat of Nylon 6 nanofibers. At the same time, the positively charged ZnO suspension was also sprayed onto the collector and ZnO nanoparticles were captured by Nylon 6 nanofibers.

Figure 2 shows photographs and FESEM images of ZnO/Nylon 6 nanofibers prepared by the electrospinning–electrospraying hybrid process and Nylon 6 nanofibers obtained solely by electrospinning. It is seen that electrospun Nylon 6 nanofibers have an average diameter of 210 ± 30 nm and are randomly deposited to form a nonwoven mat. For ZnO/Nylon 6 nanofibers, the average diameter decreases to 190 ± 40 nm, and ZnO particles were attached to the nanofiber surface and were distributed throughout the entire mat. ZnO nanoparticles are not encapsulated by the fiber matrix and are exposed to the environment. This is important for utilizing the functionalities of ZnO and achieving the high antibacterial and detoxifying activities.

3.2. Antibacterial activity of ZnO/Nylon 6 nanofiber mats

Figure 3 shows the qualitative AATCC 147 antibacterial testing results of Nylon 6 and ZnO/Nylon 6 nanofiber mats against *E. coli*. It is seen that the Nylon 6 nanofiber mat does not have antibacterial function and the bacterial streaks grow across the entire nanofiber mat from underneath. In contrast, the ZnO/Nylon 6 nanofiber mat inhibits the growth of *E. coli* and there are no bacterial streaks under and near the mat.

Quantitative antibacterial assessments were carried out using both Gram-negative *E. coli* and Gram-positive *B. cereus* bacteria. Table 2 shows the concentrations (CFU ml^{-1}) of bacterial suspensions after being treated with Nylon 6 and ZnO/Nylon 6 nanofiber mats for 24 h. The initial bacterial concentrations were 10^7 CFU ml^{-1}. It is seen that with Nylon 6 nanofiber mats, the concentrations of both *E. coli* and *B. cereus* bacteria are not significantly different from the control populations. However, for the ZnO/Nylon 6 nanofiber mats, the number of colony forming unit drops below the detection level, indicating that the ZnO/Nylon 6 nanofiber mats can effectively kill both Gram-negative and Gram-positive bacteria in 24 h. The observed reduction in bacterial cell was greater than 4 log CFU ml^{-1} indicating that the ZnO/Nylon 6 nanofiber mats have an antibacterial efficiency of at least 99.99%.

Figure 4 shows the photographs of agar plates of *E. coli* bacterial suspensions exposed to Nylon 6 and ZnO/Nylon 6 nanofiber mats for 24 h. For comparison, the photograph of the control, which was not exposed to any nanofiber

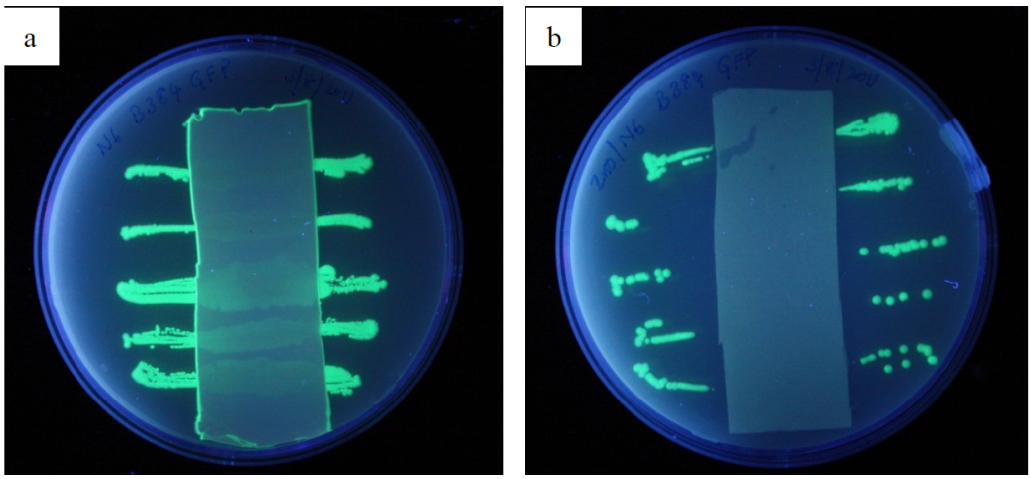

Figure 3. Agar plates with parallel streaks of green fluorescent protein (GFP) *E. coli* on: (a) Nylon 6 and (b) ZnO/Nylon 6 nanofiber mats.

Table 2. Antibacterial activities of Nylon 6 and ZnO/Nylon 6 nanofiber mats.

Sample	*E. coli* [log(CFU ml^{-1})]	*B. cereus* [log(CFU ml^{-1})]
Nylon 6 nanofiber mat	7.18	7.08
ZnO/Nylon 6 nanofiber mat	0.0	0.0

mat, is also shown. It is seen that *E. coli* bacterial colonies have spread throughout the control plate and the plate with Nylon 6 nanofiber mat, and the Q count reading showed 10^7 CFU ml^{-1}. However, for the plate containing ZnO/Nylon 6 nanofiber mat-treated bacterial suspension, the bacterial growth was below the detection range of the Q count instrument. Similar results can be seen from *B. cereus* testing plates in figure 5.

The antibacterial activity of ZnO/Nylon 6 nanofiber mats is due to the uniform presence of ZnO particles on the nanofiber surface. The antibacterial mechanism of ZnO particles has been studied and reported in literature [12]. Sawai [13] reported that in atmospheric environment, the ZnO particles could release active oxygen species which lead to the generation of hydrogen peroxide (H_2O_2) in aqueous media. H_2O_2 is capable of penetrating the bacterial cells, causing damage to the cell membranes and inhibiting the growth of or killing the bacteria. Other proposed mechanisms include release of Zn^{2+}, radical oxygen of superoxide or superoxide anions (O^{2-}), and hydroxyl radicals (OH) by the ZnO slurry [14–18]. Of these, the most likely explanation for the antibacterial activity of ZnO/Nylon 6 nanofiber mats is the presence of active radical oxygen species of superoxide anion (O^{2-}) and their strong oxidizing interactions with bacterial cells.

3.3. Detoxification of toxic chemical agent

Figure 6 shows the area counts under the peaks of GC-MS spectra obtained for the paraoxon solutions exposed to Nylon 6 and ZnO/Nylon 6 nanofiber mats. Without any nanofiber mats, the GC-MS area count of the paraoxon solution is approximately 2 million units. That area count decreases slightly for solutions exposed to Nylon 6 nanofiber mat for 15 min, indicating a small decrease in the paraoxon concentration. This concentration decrease is mainly caused by the absorption of paraoxon into the large surface area of the nanofiber mat. From figure 6, it is also seen that exposing the solution to ZnO/Nylon 6 nanofiber mat can significantly reduce the paraoxon concentration. In 15 min, the GC-MS area count decreases from ∼2 million to ∼0.1 million, indicating a detoxification efficiency of approximately 95%. After 15 min, the paraoxon concentration does not change significantly. For comparison, the GC-MS area count of paraoxon solution exposed to pure ZnO powder for 60 min is also plotted in figure 6. It is seen that the paraoxon solution exposed to ZnO powder for 60 min shows a concentration reduction that is similar to solutions exposed to ZnO/Nylon 6 nanofiber mats. Therefore, it can be concluded that the exposure of ZnO nanoparticles on the nanofiber surfaces takes full advantage of their detoxifying capabilities.

The detoxification reaction mechanism could be explained by dissociative chemisorptions of paraoxon by ZnO particles. Rajagopalan *et al* [19] proposed a destructive adsorption mechanism in which paraoxon is catalyzed by a metal oxide, which leads to the breakage of P–O bonds. Figure 7 shows the possible detoxification reaction of paraoxon by a ZnO/nylon nanofiber. Since ZnO particles are exposed on the fiber surface, they can access the paraoxon molecules and detoxify them by breaking the P–O bonds to form less harmful nitrophenol.

3.4. Air permeability and MVTR

The air permeability and MVTR values are important parameters of electrospun nanofiber mats for many applications [20, 21]. For example, in protective clothing, electrospun nanofiber mats are typically deposited onto traditional textile fabrics to provide antibacterial and/or detoxifying functions. In this case, high air permeability and good moisture vapor transmission behavior are necessary for keeping the wearers comfortable and healthy. To further

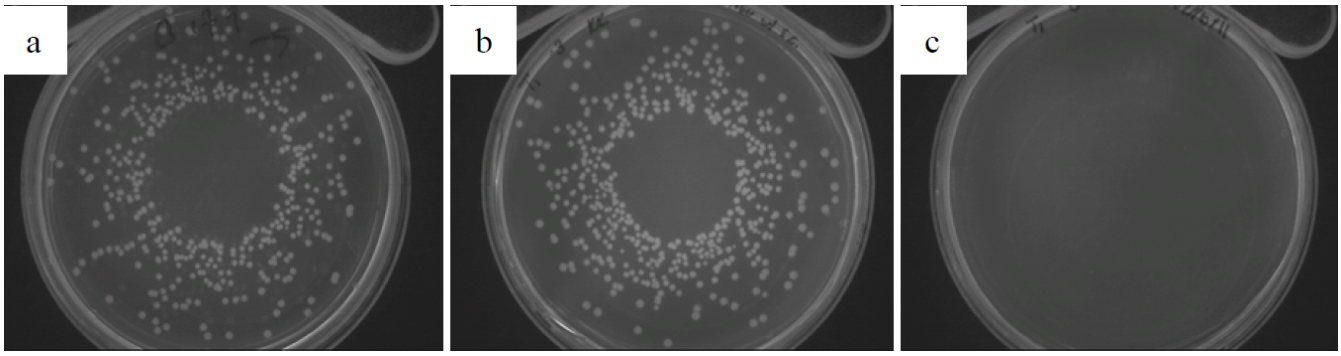

Figure 4. Agar plates of *E. coli* bacterial suspensions incubated for 24 h: (a) without nanofiber treatment, (b) treated with Nylon 6 nanofiber mat and (c) treated with ZnO/Nylon 6 nanofiber mat.

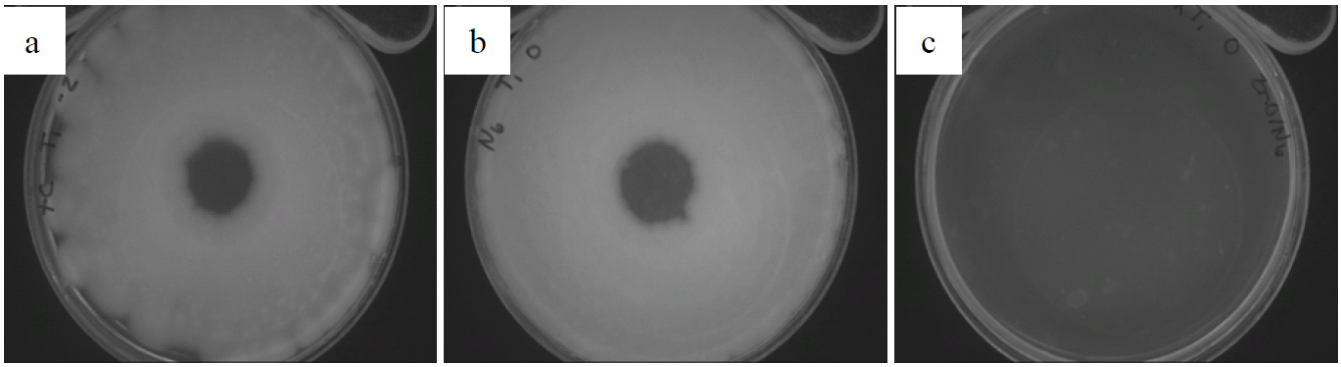

Figure 5. Agar plates of *B. cereus* bacterial suspensions incubated for 24 h: (a) without nanofiber treatment, (b) treated with Nylon 6 nanofiber mat and (c) treated with ZnO/Nylon 6 nanofiber mat.

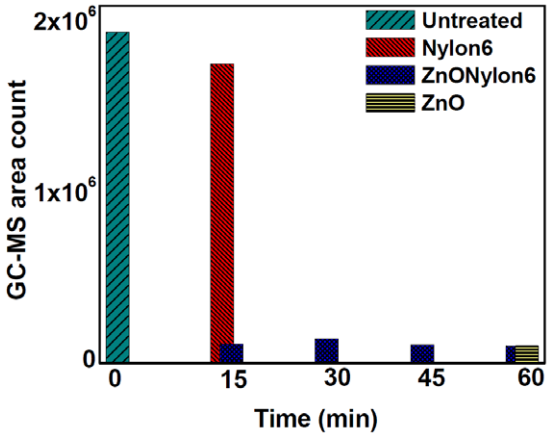

Figure 6. GC-MS area counts for paraoxon solutions treated with Nylon 6 nanofiber mat, ZnO/Nylon 6 nanofiber mat, and ZnO powder. For comparison, area count of the paraoxon solution without any treatment is shown at $t = 0$.

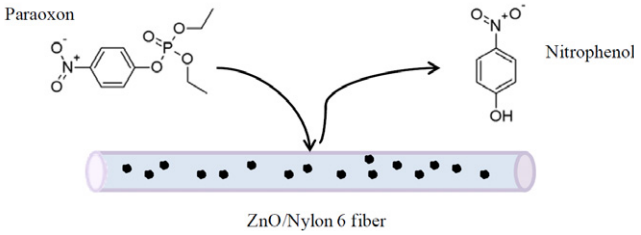

Figure 7. Possible detoxifying mechanism of paraoxon by ZnO/Nylon 6 nanofibers.

examine the feasibility of using ZnO/Nylon 6 nanofiber mats in protective applications, they were deposited onto woven nylon/cotton fabrics and the air permeability and MVTR values of the deposited fabrics were evaluated. Table 3 compares the air permeability and MVTR values obtained for the control fabric substrate and fabrics deposited with Nylon 6 and ZnO/Nylon 6 nanofiber mats. It is seen that the control fabric and the fabric coated with Nylon 6 nanofiber mat have comparable MVTR values, which indicates that the deposition of Nylon 6 nanofiber mats does not alter the moisture vapor transmission through the fabric structure. This may be due to the small fiber diameter and high porosity of the electrospun nanofiber mat. In addition, depositing a ZnO/Nylon nanofiber mat onto the fabric leads to insignificant increase in MVTR. Therefore, the presence of ZnO particles on electrospun fiber surface does not significantly affect the transmission of water vapor across the mat. From table 3, it is also seen that depositing Nylon 6 and ZnO/Nylon 6 nanofiber mats onto the fabric only slightly reduces the air permeability. However, the resultant total air permeability is still within an acceptable range for practical applications [22].

4. Summary

ZnO/Nylon 6 nanofiber mats were prepared by the electrospinning–electrospraying hybrid process.

Table 3. Moisture vapor transmission rate (MVTR) and air permeability values of Nylon 6 and ZnO/Nylon 6 nanofiber-deposited fabrics.

Sample	Nanofiber mat areal density ($g\,m^{-2}$)	MVTR [$g\,m^{-2}\,day^{-1}$]	Air permeability [m^3 air flow m^{-2} fabric min^{-1}]
Control substrate fabric	0	647 ± 17	1.082 ± 0.006
Nylon 6 nanofiber mat	3.59 ± 0.06	649 ± 34	0.905 ± 0.006
ZnO/Nylon 6 nanofiber mat	3.80 ± 0.21	654 ± 28	0.847 ± 0.006

Characterization of the nanofiber mat structure suggests that ZnO particles are distributed on the nanofiber surfaces. The capabilities of ZnO/Nylon 6 nanofiber mats to kill bacteria and detoxify chemical agents were evaluated. These mats showed powerful antibacterial activity against Gram-negative *E. coli* and Gram-positive *B. cereus* pathogens with efficiencies over 99.99%. They also exhibited good detoxifying ability against paraoxon, a simulant of toxic chemicals, with detoxification efficiency over 95%. To further examine the feasibility of using ZnO/Nylon 6 nanofiber mats in protective applications, they were deposited onto woven nylon/cotton fabrics, and the air permeability and MVTR values of nanofiber mat-deposited fabrics were acceptable for practical uses. Therefore, ZnO/Nylon 6 nanofiber mats prepared by the electrospinning–electrospraying hybrid process have effective antibacterial and detoxifying functions without sacrificing air permeability and MVTR values, which is highly desirable in protective applications.

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