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PAPER

One-step synthesis of silver nanoparticle-filled nylon 6 nanofibers and their antibacterial properties

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A novel and facile one-step approach to *in situ* synthesize silver nanoparticle-filled nylon 6 nanofibers by electrospinning is reported. The method does not need post-treatments and can be carried out at ambient conditions without using additional chemicals. It employs the electrospinning solvent as a reducing agent for *in situ* conversion of $AgNO_3$ into silver nanoparticles during the solution preparation. The resultant silver nanoparticle-filled nylon 6 hybrid nanofibers show an excellent fibrous structure (fiber diameter at 50–150 nm), with narrow size 2–4 nm silver nanoparticles uniformly dispersed throughout the nylon 6 matrix. DSC analysis shows that the *in situ* incorporation of silver nanoparticles increased the T_g and crystallinity of the resultant nanofibers. These silver nanoparticle-filled nylon 6 nanofibers exhibit a steady and long-lasting silver ion release behavior, and robust antibacterial activity against both Gram-positive *B. cereus* and Gram-negative *E. coli* microorganisms.

Introduction

Electrospinning is a versatile and reliable method to produce polymer nanofibers with ultrahigh surface-area-to-volume ratios and outstanding properties that overcome the limitations of conventional fibers and non-woven mats.[1–3] Recently, there has been great interest in the unique mechanical, electrical, chemical and optical properties that can be achieved by combining the advantages of metal nanoparticles and polymer nanofibers.[4–8] Such hybrid nanofibers have applications in a wide range of areas, *e.g.*, energy storage,[9] biomedical materials,[10] catalysis,[11] and sensors.[12] The properties of these hybrid nanofibers depend not only on the content and size of the metal nanoparticles, but also on their spatial distribution.[13–15] However, metal nanoparticles often have the tendency to aggregate in the polymer matrix during nanofiber formation. Hence, a facile and feasible approach to attain good dispersion of metal nanoparticles in the polymer nanofiber matrix is highly desirable.

Traditionally, metal nanoparticle-filled polymer nanofiber composite materials are prepared by a two-step process in which nanoparticles are synthesized and dispersed into the electrospinning solution.[16,17] The two-step process suffers from the following shortcomings: (1) protecting or stabilizing agents are often required to prevent the nanoparticles from aggregating during the solution preparation;[18,19] (2) the prepared nanoparticles need to be extracted or purified before use;[20] (3) dispersion of nanoparticles in electrospinning solution is challenging due to the high viscosity of most ready-to-spin polymer solutions.[21] Hence, to eliminate the usage of additional chemicals, minimize the time and energy consumption, and obtain sustainability, there is significant interest in developing single-step processes, *e.g.*, using metal salt as the nanoparticle precursor and reducing the salt into metal nanoparticles during solution preparation or nanofiber formation to obtain good particle dispersion in the matrix.[22,23] The key objective is to find a clean, convenient and feasible method to process the *in situ* reduction without affecting the structure and properties of resultant nanofibers.

It has been reported that one-step preparation of nanoparticle-filled polymer nanofibers can be realized by combining electrospinning with chemical treatment,[24,25] irradiation,[26,27] thermal treatment,[28,29] or some other methods.[30] However, many of these methods are time and energy consuming. In addition, they often utilize chemicals that are highly toxic. Recently, researchers tried to use the electrospinning polymer as the reducing agent to convert metal salts into metal nanoparticles. For example,

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Saquing *et al.* reported one-step synthesis of silver nanoparticle-filled polyethylene oxide (PEO) electrospun nanofibers.[31] They found that high-molecular weight PEO formed pseudo-crown ethers with silver ions and reduced them into silver nanoparticles at ambient conditions.[32] In addition to PEO, polyvinylpyrrolidone (PVP) has also been reported to have the ability to reduce silver/gold ions into silver/gold nanoparticles.[33,34]

In this paper, we describe for the first time preparation of silver nanoparticle-filled polymer nanofibers by using the electrospinning solvent as a reducing agent and the electrospinning polymer as a stabilizing agent. Nylon 6 is selected as the polymer matrix since it is one of the most commonly used textile materials. Formic acid is used as both the electrospinning solvent and reducing agent because of the presence of reducing aldehyde groups in its molecular structure. The surface morphology, nanoparticle dispersion, thermal and antibacterial properties of the resultant hybrid nanofibers were studied systematically.

Experimental

Materials

Nylon 6 ($T_g = 62.5$ °C), formic acid, and silver nitrate ($AgNO_3$) were purchased from Sigma-Aldrich Co. Ltd (St Louis, MO). All agents were used without further purification.

Preparation of nylon 6/silver electrospinning solution

Nylon 6 was dissolved in formic acid at a concentration of 15 wt % and was stirred at 50 °C for 6 hours to obtain a transparent homogeneous solution. The solution was then cooled to room temperature under stirring, and a calculated amount of $AgNO_3$ (0.5 or 1.25 wt% in solution) was slowly added. The solution was kept away from light and stirred under room temperature for 24 hours to ensure the complete reduction of $AgNO_3$.

Electrospinning

The ready-to-electrospin solution was collected in a 10 ml syringe equipped with a 24 gauge stainless steel needle tip. The syringe was fixed on an electric syringe pump set to maintain a constant feed rate of 1.0 ml h^{-1}. Positive charge was applied to the needle by a high-voltage power supply (Gamma ES40P-20W/DAM). A grounded metal plate covered with aluminium foil served as the collector. The voltage used for electrospinning was 20 kV. The distance between the needle tip and the collector was 15 cm. Pure nylon 6 solution was also electrospun into nanofibers to be used as the control.

Characterizations and measurements

Solution viscosity was measured by a DV-II Brookfield digital viscometer (Brookfield Engineering Laboratories, Inc., Middleboro, MA). Solution conductivity was measured using an AP85 conductivity meter (Fisher Scientific, Inc). Surface morphology of nanofibers was observed using a JEOL JSM-6400F Field Emission Scanning Electron Microscope (SEM) (JEOL Ltd, Tokyo, Japan) with an accelerating voltage of 15 kV. The size and distribution of silver nanoparticles inside the nanofibers were observed using a Hitachi HF-2000 Transmission Electron Microscope (TEM) (Hitachi High Technologies America, Inc., Schaumburg, IL) with an accelerating voltage of 20 kV.

Silver ion release

Silver ion release behavior of the nanofibers was determined by atomic adsorption spectrometry (AAS). A small piece of electrospun nanofiber mat (approximately 50 mg) was placed in a glass container, and 25 ml deionized water was added into the container as the release medium. The container was shaken to make sure the nanofiber mat was completely immersed, then sealed and incubated at 37 °C. The deionized water was collected every 24 hours and replaced by the same volume of fresh water. Silver ion concentration in the solution was measured using a Perkin-Elmer AA300 atomic adsorption spectrometer (PerkinElmer Inc. Waltham, MA).

Antibacterial assessment assay

Escherichia coli O157:H7 (B179), a Gram-negative enteric pathogen, and *Bacillus cereus* (B002), a spore-forming Gram-positive pathogen, were obtained from the Food Science Research Unit Culture Collection (FSRU-USDA-ARS, Raleigh, NC). *E. coli* B179 was propagated on Luria–Bertani (LB) agar and broth (BD Company, Sparks, MD) and *B. cereus* B002 was propagated on TSA agar and broth (BD Company, Sparks, MD). To prepare cells for antimicrobial fiber assays, 5 ml broth cultures were inoculated into LB broth and TSA broth (for *E. coli* and *B. cereus*, respectively) from individual colonies on an agar plate, and then incubated for 18 hours at 37 °C on a shaker platform at 200 rpm (Eppendorf Thermomixer; Hamburg, Germany). Following the incubation, cells were harvested by centrifugation (5000 × *g*, 10 min, 4 °C, Sorvall RB-5C centrifuge) and re-suspended in an equal volume of physiological saline (0.85% NaCl). Cells were diluted to 1×10^7 CFU (colony forming units) per ml and used immediately for testing.

Nanofiber mats were cut into small pieces (5–8 mg) and separately placed in 1.5 ml microcentrifuge tubes. The saline cell suspension (200 μL) containing approximately 1×10^7 CFU per ml of the test organism was placed in the tubes, completely covering nanofiber mat samples. A positive control (cell suspension in saline with no nanofibers) and two negative controls (saline only and saline with pure nylon 6 nanofibers) were also included in the experimental design. The nanofiber mat samples were incubated for 24 hours at 37 °C with gentle agitation at 300 rpm on a shaker platform (Eppendorf Thermomixer; Hamburg, Germany). After 24 hours, LB (*E. coli*) and TSA (*B. cereus*) agar plates were spread to enumerate surviving cells using a spiral plater (Model 4000, Spiral Biotech, Norwood, MA). After overnight incubation (18 hours at 37 °C), bacterial colonies on plates were counted using an automated spiral plate reader (Q-count, Spiral Biotech, Norwood, MA).

Results and discussion

In situ reduction of silver nitrate

It is well known that $AgNO_3$ can be reduced into metallic silver by reductive aldehyde groups. The formic acid in this system acts not only as the solvent for nylon 6 but also as a reducing agent

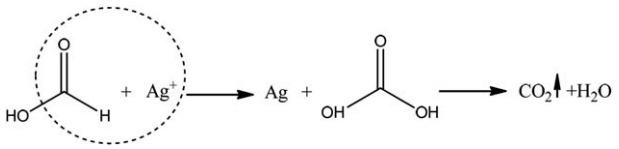

Fig. 1 Chemical mechanism of silver reduction by formic acid.

Table 1 Properties of $AgNO_3$/nylon 6 solutions with different $AgNO_3$ concentrations

	Nylon 6	0.5% $AgNO_3$/ nylon 6	1.25% $AgNO_3$/ nylon 6
Viscosity/cp	406 ± 5	443 ± 6	466 ± 3
Conductivity/ ms cm^{-1}	5.08 ± 0.03	4.65 ± 0.02	4.77 ± 0.03

for $AgNO_3$. The nylon 6 solution in formic acid, followed by the addition of silver nitrate, gradually turned opaque and dark, with visible bubbles observed. This can be explained by the reaction mechanism shown in Fig. 1. When silver nitrate is added into the formic acid solution of nylon 6, it is reduced into metallic silver by the aldehyde group in formic acid molecule. At the same time, the aldehyde group is oxidized into carboxyl group to form carbonic acid, which is unstable and quickly dissociates into carbon dioxide and water.

The most notable feature of this approach is the *in situ* stabilization of silver nanoparticles. When the silver ions are reduced into metallic silver, the silver atoms first aggregate into clusters. The clusters are very small in size and have extremely high surface energy, which drives them to aggregate into larger particles. In many cases, a surfactant is added into the synthesis system to stabilize silver nanoparticles and prevent them from further aggregating.[35,36] In this research work, as shown in Fig. 2, the reduction reaction occurs in nylon 6 solution with formic acid as the reducing agent. Once the silver nanoparticles are formed, nylon 6 molecules on the particle surface stabilize them in nanosize and keep them from further aggregating by reducing their surface energy. Here the nylon 6 molecules act as both the matrix of electrospun nanofibers and the stabilizing agent of silver nanoparticles. The mechanism will be further discussed and supported in following sections.

Electrospinning and characterization of silver nanoparticle-filled nylon 6 nanofibers

Table 1 shows the viscosities and conductivities of electrospinning solutions with different $AgNO_3$ precursor

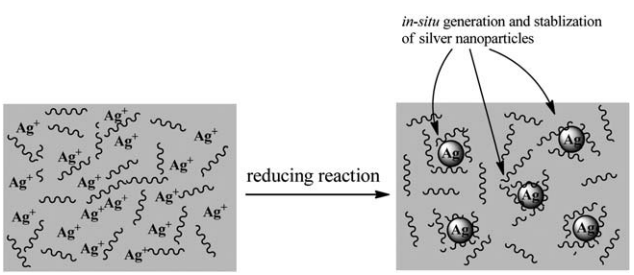

Fig. 2 *In situ* generation and stabilization of silver nanoparticles.

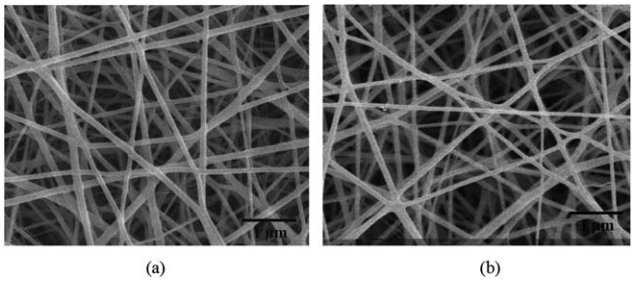

Fig. 3 SEM images of silver nanoparticle-filled nylon 6 nanofibers electrospun from (a) 0.5% and (b) 1.25% $AgNO_3$/nylon 6 solutions.

concentrations. It is seen that the solution viscosity increased with the addition of $AgNO_3$ precursor and at the same time, the conductivity decreased. As shown in Fig. 2, each silver nanoparticle binds with a layer of nylon 6 molecules on its surface due to the high particle surface activity. The nylon 6 molecule chains on the surface of silver nanoparticles form intermolecular interactions with chains in the solution, which is responsible for the viscosity increase.[37] The addition of $AgNO_3$ should have increased the conductivity of solution because of the existence of the Ag^+ and NO_3^- ions. However, after the reduction reaction the Ag^+ ions were converted into Ag nanoparticles and covered by nylon molecules, leading to reduced conductivity.

Fig. 3 demonstrates the surface morphology of nanofibers electrospun from $AgNO_3$/nylon 6 solutions (after reduction reaction). All nanofibers show a continuous and smooth fibrous structure, with diameters from 50 to 150 nm. The average diameter of nanofibers with higher silver content is slightly thinner than those with lower silver content. Shown in Fig. 4 are TEM images of nanofibers electrospun from 1.25% $AgNO_3$/nylon 6 solution. From these images, it is seen that silver nanoparticles were embedded in the nylon 6 matrix and dispersed uniformly throughout the nanofiber structure. In addition, the size distribution of silver nanoparticles is also narrow. As shown in Fig. 4, the diameters of most silver nanoparticles are in the range of 2–4 nm. Both the narrow size distribution of nanoparticles and their uniform particle distribution in fiber matrix are the results of the *in situ* generation of silver nanoparticles and the stabilization effect of nylon 6 molecules.

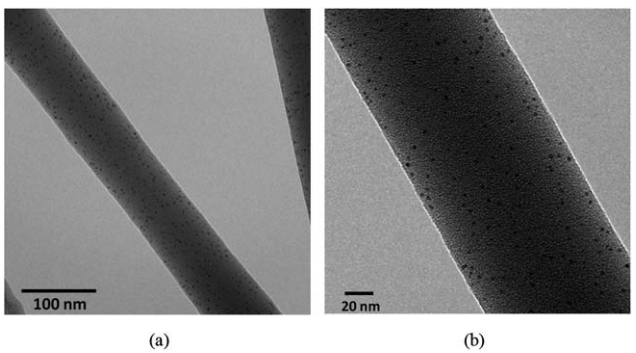

Fig. 4 TEM images of silver nanoparticle-filled nylon 6 nanofibers electrospun from 1.25% $AgNO_3$/nylon 6 solution. (a) 50 000×, and (b) 100 000×.

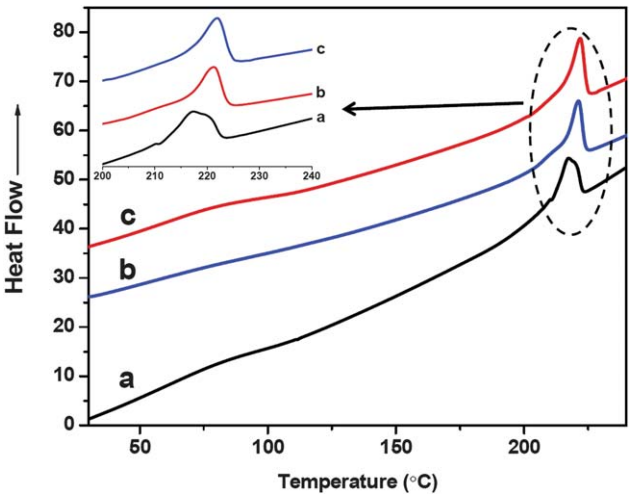

Fig. 5 DSC thermograms of nanofibers electrospun from (a) pure nylon 6, (b) 0.5% $AgNO_3$/nylon 6, and (c) 1.25% $AgNO_3$/nylon 6 solutions.

Table 2 Thermal properties of nanofibers electrospun from nylon 6 and $AgNO_3$/nylon 6 solutions

	Nylon 6	0.5% $AgNO_3$/ nylon 6	1.25% $AgNO_3$/ nylon 6
T_g/°C	63.2	68.0	71.9
T_m/°C	217.9	221.9	222.6
Melting ΔH/J g^{-1}	58.3	64.2	67.6

DSC thermograms of silver nanoparticle-filled nanofibers are shown in Fig. 5. The T_g, T_m and melting ΔH values are listed in Table 2. From Fig. 5 and Table 2, it is seen that T_g of nanofibers increased with the *in situ* incorporation of silver nanoparticles and with the increase of silver content. This indicates the silver nanoparticles can form interactions with polymer chains and then hinder their movements when temperature increases, so as to increase T_g. The same trends can be observed on T_m and melting ΔH, which means the *in situ* incorporation of silver nanoparticles results in a higher crystallinity. Melting peaks of silver nanoparticle-filled nanofibers are showing more smooth and regular shape than those of pure nylon nanofibers (as shown in the inset of Fig. 5). This is probably because that the *in situ* generated silver nanoparticles, after absorption of nylon 6 molecules, acted as nuclei sites in the solidifying process, so as to induce the crystallization.

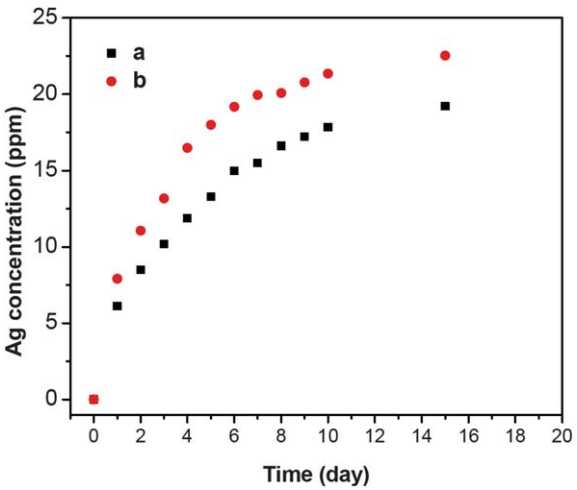

Fig. 6 Silver release profiles of silver nanoparticle-filled nylon 6 nanofibers electrospun from (a) 0.5% and (b) 1.25% $AgNO_3$/nylon 6 solutions.

Table 3 Antibacterial activities of silver nanoparticle-filled nylon 6 nanofibers electrospun from nylon 6 and $AgNO_3$/nylon 6 solutions

	Nylon 6	0.5% $AgNO_3$/ nylon 6	1.25% $AgNO_3$/ nylon 6
Gram (+) (*B. cereus*) (log reduction)	0.2	3.4	3.4
Gram (−) (*E. coli*) (log reduction)	0.1	4.0	5.8

Silver ion release

One of the most important parameters to evaluate silver-based antibacterial materials is the silver ion release rate. It was reported that a steady and prolonged silver ion release rate at a concentration level as low as 0.1 part per billion is necessary to provide effective antibacterial properties.[38] In this work, the silver ion release behavior of silver-nanoparticle-filled nanofibers was studied using AAS spectra. When the nanofiber mats are immersed into aqueous solution, the silver nanoparticles gradually release silver ions into the water. The release rate is mainly determined by the content of silver nanoparticles and the diffusion distance from inside the fiber to the surface. Silver release profiles of silver nanoparticle-filled nanofibers are shown in Fig. 6. It is seen that the release rate is relatively high in the first few days and then decreases and levels off over time. The cumulative releases over 15 days for the nanofibers electrospun from 0.5% and 1.25% $AgNO_3$/nylon 6 solutions were approximately 18 and 25 ppm, respectively. After 10 days, the nanofibers still gave a steady release rate at 0.5–1 ppm per day. The results indicate that silver nanoparticle-filled nylon 6 nanofibers prepared by the one-step process can release sufficient amounts of silver to exhibit sustained antibacterial activity.

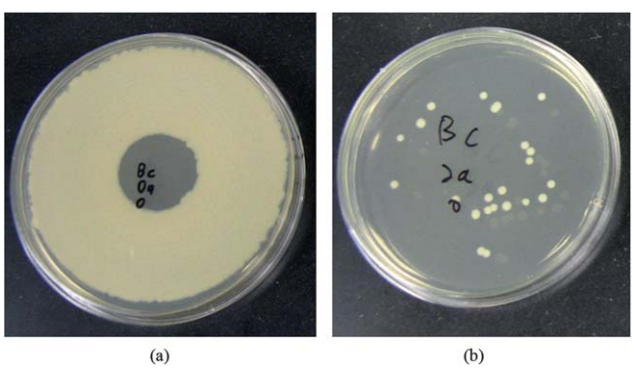

Fig. 7 Antibacterial test plates of *B. cereus* treated with (a) pure nylon 6 and (b) silver nanoparticle-filled nylon 6 nanofibers. $AgNO_3$ precursor concentration: 1.25%.

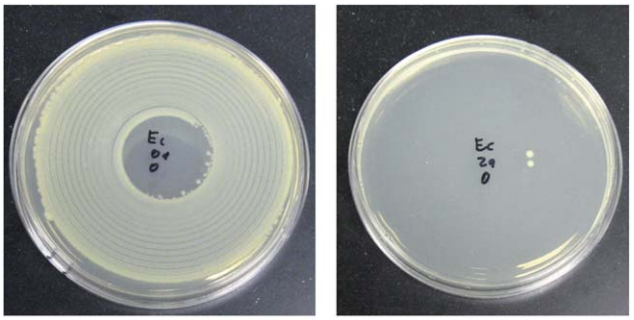

Fig. 8 Antibacterial test plates of *E. coli* treated with (a) pure nylon 6, and (b) silver nanoparticle-filled nylon 6 nanofibers. $AgNO_3$ precursor concentration: 1.25%.

Antibacterial assay

Antibacterial properties of silver nanoparticle-filled nylon 6 nanofibers were tested on both Gram-positive *B. cereus* and Gram-negative *E. coli* microorganisms. The positive control (microorganism without any nanofiber treatment) had 1×10^6 to 1×10^7 colony forming units (CFU) per ml. The positive control cultures were then treated with different nanofibers and incubated for 24 h to count the number of CFU per ml. The results are shown in Table 3, expressed as the logarithmic decrease (log reduction) of CFU per ml as compared with the positive control. For comparison, results for pure nylon 6 nanofibers are also shown.

From Table 3, it is seen that pure nylon 6 nanofibers did not show significant antibacterial activity. By contrast, silver nanoparticle-filled nylon 6 nanofibers have excellent bactericidal efficiency to both *B. cereus* and *E. coli.* In the case of *B. cereus*, nanofibers electrospun from 0.5 and 1.25% $AgNO_3$/nylon 6 solutions both showed 3.4 log reduction, indicating over 99.9% inhibition. In the case of *E. coli*, nanofibers electrospun from 0.5% $AgNO_3$/nylon 6 solution showed a 4.0 log reduction (around 99.99% inhibition) while those from 1.25% $AgNO_3$/nylon 6 hybrid nanofibers showed a 5.8 log reduction (almost 99.9999% inhibition). Photographs of agar plates plated with the cell suspension treated with pure nylon 6 and silver nanoparticle-filled nylon 6 nanofibers (prepared from 1.25% $AgNO_3$/nylon 6 solution) are shown in Fig. 7 and 8, respectively, for Gram-positive and Gram-negative microorganism tests. It can be concluded that silver nanoparticle-filled nylon 6 nanofibers prepared by the one-step process have excellent antibacterial properties against both Gram-positive and Gram-negative microorganisms.

Conclusion

This paper describes a facile approach to fabricate silver nanoparticle-filled nylon 6 hybrid nanofibers *via* a one-step electrospinning process. The method features the novelty of using electrospinning solvent as the reducing agent and polymer matrix as the stabilizing agent for the *in situ* synthesis of silver nanoparticles. Besides the electrospinning solution, this method does not need additional reducing/protecting agents, or thermal/irradiation treatment. The *in situ* generation of nanoparticles and the stabilizing mechanism of nylon 6 molecules result in narrow size distribution of silver nanoparticles and uniform dispersion of silver nanoparticles in the nanofiber matrix, as analyzed by SEM and TEM. Characterization by DSC indicates that silver nanoparticles have strong interaction with nylon 6 polymer chains. The resultant silver nanoparticle-filled nylon 6 nanofibers provide a steady and prolonged silver ion release. Antibacterial assays show these nanofibers have over 99.9% inhibition efficiency to *B. cereus* and almost 99.9999% to *E. coli*.

Acknowledgements

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