European Polymer Journal 47 (2011) 1402–1409

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

MACROMOLECULAR NANOTECHNOLOGY

Macromolecular Nanotechnology

Durable antibacterial Ag/polyacrylonitrile (Ag/PAN) hybrid nanofibers prepared by atmospheric plasma treatment and electrospinning

Quan Shi [a], Narendiran Vitchuli [a], Joshua Nowak [b], Jane M. Caldwell [c,d], Frederick Breidt [c,d], Mohamed Bourham [b,*], Xiangwu Zhang [a,*], Marian McCord [a,e,f,*]

[a] Fiber and Polymer Science Program, Department of Textile Engineering, Chemistry and Science, North Carolina State University, Raleigh, NC 27695-8301, USA
[b] Department of Nuclear Engineering, North Carolina State University, Raleigh, NC 27695-7909, USA
[c] US Department of Agriculture, Agricultural Research Service, North Carolina State University, Raleigh, NC 27695-7624, USA
[d] Department of Food Science, North Carolina Agricultural Research Service, North Carolina State University, Raleigh, NC 27695-7624, USA
[e] Joint Department of Biomedical Engineering, North Carolina State University, Raleigh, NC 27695-7115, USA
[f] University of North Carolina, Chapel Hill, NC 27599, USA

ARTICLE INFO

Article history:
Received 26 January 2011
Received in revised form 3 April 2011
Accepted 7 April 2011
Available online 16 April 2011

Keywords:
Atmospheric plasma
Electrospinning
Nanofibers
Ag nanoparticles
Antibacterial activity

ABSTRACT

Durable antibacterial Ag/polyacrylonitrile (Ag/PAN) hybrid nanofibers were prepared by atmospheric plasma treatment and electrospinning. Atmospheric helium plasma treatment was first used to reduce the $AgNO_3$ precursor in pre-electrospinning solutions into metallic silver nanoparticles, followed by electrospinning into continuous and smooth nanofibers with Ag nanoparticles embedded in the matrix. SEM, TEM, and EDX spectra were used to study the structure and surface elemental composition of the nanofibers. Silver nanoparticles, with diameters ranging between 3 and 6 nm, were found to be uniformly dispersed in the nanofiber matrix. The Ag/PAN nanofibers exhibited slow and long-lasting silver ion release, which provided robust antibacterial activity against both Gram-positive *Bacillus cereus* and Gram-negative *Escherichia coli* microorganisms.

1. Introduction

In the past few years, silver-containing electrospun nanofibers have attracted interest as a novel form of antimicrobial material [1,2]. Electrospinning is a well-established process for fabrication of nanofiber mats with high surface areas, large volume-to-mass ratios, and high porosities [3–5]. This process has been demonstrated to be suitable for manufacturing scale-up for low-cost mass production [6,7]. Silver is a widely-used and recognized broad-spectrum biocidal agent that is effective against bacteria, fungi and viruses but is non-toxic to human cells [8–12]. Polymer matrices loaded with silver nanoparticles have been used in numerous applications including wound dressings [13], tissue scaffolds [14], chemical and biological protective materials [15], and medical devices and biotextiles [16,17]. The combination of the high specific surface area and fineness of electrospun nanofibers with the biocidal activity of Ag nanoparticles results in a superior and versatile antimicrobial material [18–20].

The simplest and most-commonly used method for combining Ag nanoparticles with electrospun nanofibers is by suspension of Ag nanoparticles directly into the pre-electrospinning polymer solutions [21,22]. However, nanofibers produced using this method have demonstrated diminished antimicrobial efficiency due to Ag nanoparticle aggregation and subsequent reduced bioavailability. *In situ* reduction of silver ions in pre-electrospinning solutions results in a more uniform dispersion of Ag nanoparticles, partially as a result of the stabilizing effect of polymer molecules [23,24]. Reduction of silver nitrate in polymer solutions or polymer matrices by hydrogen gas [1], hydrazinium hydroxide [25], borohydride [26], citrate [27], and ascorbate [28] has been reported. In order to avoid the

* Corresponding authors.
E-mail addresses: bourham@ncsu.edu (M. Bourham), xiangwu_zhang@ncsu.edu (X. Zhang), mmccord@ncsu.edu (M. McCord).

0014-3057/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.eurpolymj.2011.04.002

use of environmentally hazardous or dangerous chemical agents, a series of environmentally sustainable "green synthesis" methods, are under investigation [29]. These methods include the polysaccharide method (synthesis of silver nanoparticles by nanoscopic starch templates) [30], irradiation method (radiolysis of silver nanoparticles by microwave, pulse, and gamma irradiation) [31], and biological method (synthesis of silver nanoparticles by a special plant extract, bio-organism extract, or even certain microorganisms) [32]. However, these "green" methods typically require longer treatment times and additional procedures to incorporate Ag nanoparticles into polymer matrices [33–35]. Hence, it is still a great challenge to develop *in situ*, fast and environmentally friendly methods to fabricate Ag nanoparticle-containing nanofibers.

Atmospheric plasma treatment is currently being employed for chemical modification of polymer materials due to its low cost, good environmental sustainability, high efficiency, and low energy consumption [36–38]. Within a typical inert gas plasma process, gas molecules are dissociated to ions, electrons and excited atoms [39,40]; this chemical environment is ideal for silver reduction. Moreover, during the gas breakdown, atmospheric plasma generates UV irradiation [41,42], another reducing agent for photosensitive silver salts. However, to date, there are no reports of the use of atmospheric plasma treatment to prepare Ag nanoparticle composite materials.

This paper reports on a novel and efficient method that combines atmospheric plasma treatment and electrospinning to produce silver nanoparticle/polymer hybrid nanofibers. Polyacrylonitrile (PAN) was chosen as the polymer matrix. Atmospheric plasma treatment was applied to solutions of PAN and $AgNO_3$ to generate Ag nanoparticles prior to electrospinning. The surface and bulk morphologies and antibacterial effectiveness and duration of the resultant Ag/PAN hybrid nanofibers were systematically investigated.

2. Experimental

2.1. Materials and solution preparation

Polyacrylonitrile (PAN, M_w = 1,500,000), *N*,*N*-dimethylformamide (DMF) and silver nitrate ($AgNO_3$) were purchased from Sigma–Aldrich Co. Ltd. (St. Louis, MO). All these reagents were used without further purification.

PAN was dissolved in DMF at a concentration of 8 wt.% and stirred at 60 °C for 6 h to obtain a transparent homogenous solution. Then, the solution was cooled to room temperature, and a calculated amount of $AgNO_3$ (0.5 or 1.25 wt.% in solution) was added. The blend solution was shielded from light and stirred for another 2 h to ensure the complete dissolution of $AgNO_3$.

2.2. Atmospheric plasma treatment

Atmospheric plasma treatment of the $AgNO_3$/PAN solution was carried out in a capacitively-coupled dielectric barrier discharge atmospheric pressure plasma system (Fig. 1). The device has an active exposure area of $60 \times 60\ cm^2$ between two copper electrodes. The plasma was operated by a 4.8 kW audio frequency power supply at 1–10 kHz [43–45]. Ten milliliter of $AgNO_3$/PAN solution was added to a petri dish with a liquid depth of approximately 5 mm. The petri dish was placed directly in the middle of lower electrode plate for plasma treatment, as shown in Fig. 1. The treatment was carried out in helium atmospheric plasma discharge for up to 5 min.

2.3. Electrospinning

The plasma-treated solution was immediately collected into 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 1.5 ml/h. A high-voltage power supply (Gamma ES40P-20 W/DAM) was employed to apply positive charge to the needle, and a grounded metal plate covered with aluminum foil served as the collector. The voltage used for electrospinning was 20 kV. The distance between the needle tip and collector was 20 cm. Pure PAN solution and untreated PAN/$AgNO_3$ solution were also electrospun into nanofibers to be used as controls. After electrospinning, all nanofibers were folded in aluminum foil and stored in a dark container to avoid the exposure to visible light and UV irradiation.

2.4. Characterizations and measurements

Solution viscosity was measured by DV-II Brookfield digital viscometer (Brookfield Engineering Laboratories,

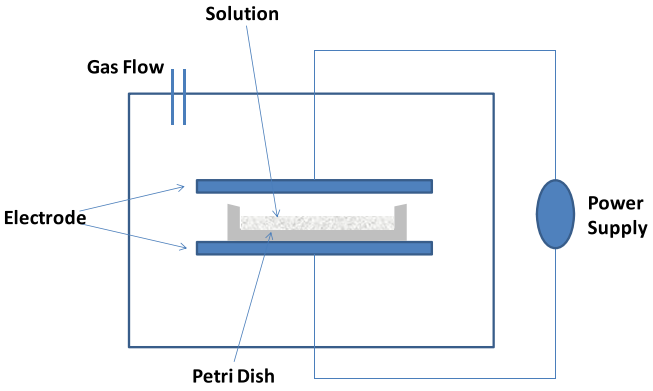

Fig. 1. Schematic diagram of plasma treatment setup.

Inc., Middleboro, MA). Solution conductivity was measured using an AP85 conductivity meter (Fisher Scientific, Inc., Pittsburgh, PA). 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 Ag nanoparticles inside the nanofibers were observed using a Hitachi HF-2000 Transmission Electron Microscopy (TEM) (Hitachi High Technologies America, Inc., Schaumburg, IL), with an accelerating voltage of 20 kV.

2.5. Silver ion release

Silver ion release behavior of the Ag/PAN hybrid 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 sealed and agitated to insure complete immersion of the nanofiber mat, and then incubated at 37 °C. The deionized water was collected every 24 h, and silver ion concentration in the solution was measured using a Perkin-Elmer AA300 AA spectrometer (PerkinElmer Inc., Waltham, MA).

2.6. 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 or TSA broth (for *E. coli* and *B. cereus*, respectively) from individual colonies on an agar plate, and then incubated for 18 h 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 resuspended in an equal volume of physiological saline (0.85% NaCl). Cells were diluted to 1×10^7 colony forming units (CFU)/mL and used immediately for testing.

Nanofiber mats were cut into small pieces (5–8 mg) and separately placed into 1.5 ml microcentrifuge tubes. The saline cell suspension (200 μL) containing approximately 1×10^7 CFU/ml of the test organism was pipetted into 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 PAN nanofibers) were also included in the experimental design. The nanofiber mat samples were incubated for 24 h at 37 °C with gentle agitation at 300 rpm on a shaker platform (Eppendorf Thermomixer; Hamburg, Germany). After 24 h, LB (*E. coli*) or 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 h at 37 °C), bacterial colonies on plates were counted using an automated spiral plate reader (Qcount, Spiral Biotech, Norwood, MA).

3. Results and discussion

3.1. Plasma reduction of silver

Transformation from silver ions to Ag nanoparticles in solutions could be observed visibly as a color change before and after plasma treatment (Fig. 2). Untreated $AgNO_3$/PAN solution is colorless and transparent, as shown in Fig. 2a, because the silver exists in the form of Ag^+ ions. Reduction of Ag^+ to Ag(0) results in a darker color due to the generation of metallic Ag nanoparticles. Fig. 2b–f shows $AgNO_3$/PAN solutions treated with atmospheric plasma for different exposure times. It is clear that the solution color gradually turns darker with increased durations of atmospheric plasma exposure. After 5 min, Ag^+ ions have been reduced into metallic Ag nanoparticles, and the solution exhibits a deep brown color.

Fig. 3 is a schematic representing the mechanism for the *in situ* formation of Ag nanoparticles by atmospheric plasma. Atmospheric plasma is a highly ionized state of matter containing a large number of electrons. Silver ions in a plasma medium can be reduced by these electrons. UV irradiation generated by the plasma discharge is also a substantial source for reduction of the photo-sensitive silver salts. Synergistic effects of electrons and UV irradiation make atmospheric plasma treatment a more effective and

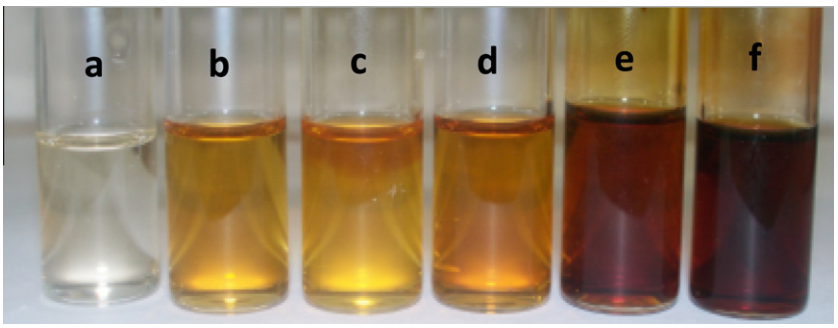

Fig. 2. $AgNO_3$/PAN solutions treated by atmospheric plasma for: (a) 0, (b) 1, (c) 2, (d) 3, (e) 4, and (f) 5 min.

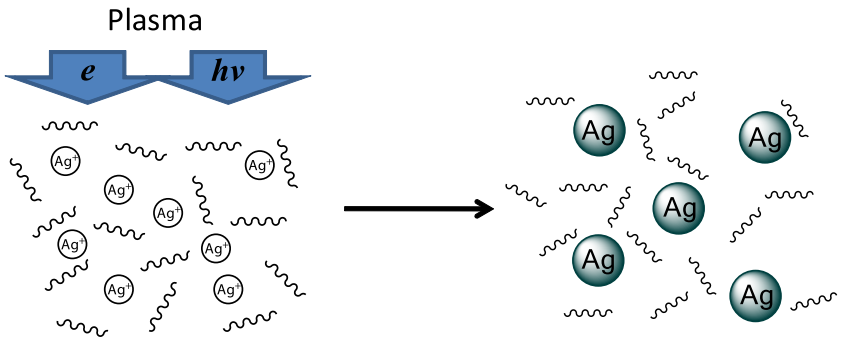

Fig. 3. Schematic diagram of plasma-reducing process.

Table 1
Conductivities and viscosities of PAN/$AgNO_3$ solutions.

	0.5% $AgNO_3$/PAN Un-treated	0.5% $AgNO_3$/PAN Plasma-treated	1.25% $AgNO_3$/PAN Un-treated	1.25% $AgNO_3$/PAN Plasma-treated
Conductivity (μs/cm)	426 ± 4	527 ± 3	849 ± 5	924 ± 3
Viscosity (cp)	746 ± 2	784 ± 5	792 ± 2	826 ± 3

fast approach to form well-dispersed Ag nanoparticles in polymer solutions [19,46,47].

3.2. Formation of Ag/PAN nanofibers

Table 1 shows the properties of $AgNO_3$/PAN solutions with different $AgNO_3$ concentrations (wt.% in the entire solution) before and after plasma treatment. It is seen that the $AgNO_3$ concentration is positively correlated with solution conductivity [48]. The solution conductivity also increases after plasma treatment due to the transition from silver ions to metallic silver. Solution viscosity increases with the addition of $AgNO_3$. After plasma treatment, the solution viscosity also increases slightly, due to the formation of Ag nanoparticles.

SEM images of nanofibers electrospun from plasma-treated solutions are shown in Fig. 4. It is seen that Ag/PAN hybrid nanofibers are smooth and continuous, with diameters in the range of 200–600 nm. At higher Ag concentration, the diameters of electrospun nanofibers are slightly smaller than those prepared at lower concentrations. This is because at a higher Ag concentration, the solution conductivity is higher and the electrospun filament is attenuated more by the electric field during electrospinning process.

Fig. 5a shows a high-magnification SEM image of Ag/PAN hybrid nanofibers, in which the Ag nanoparticles can be observed on the surface of the nanofibers. Fig. 5b shows the EDX spectra of these nanofibers. The peak for elemental Ag is additional evidence for the formation of Ag nanoparticles.

The distribution of Ag nanoparticles in the Ag/PAN hybrid nanofibers was further observed under TEM (Fig. 6). It is seen that Ag nanoparticles are uniformly dispersed across the entire nanofiber matrix. Most of the nanoparticle diameters range between 3 and 6 nm (Fig. 6b).

3.3. Silver ion release

For silver-based antibacterial materials, the most critical factor is the silver release behavior, which can inhibit the growth of bacteria. It has been reported that a steady and prolonged release of silver at a concentration level as low as 0.1 part per billion (ppb) can render effective antimicrobial activity [49]. In this work, silver release rates of Ag/PAN nanofibers were investigated in deionized water. In an aqueous environment, the Ag nanoparticles embedded in the nanofibers are released into the solution in form

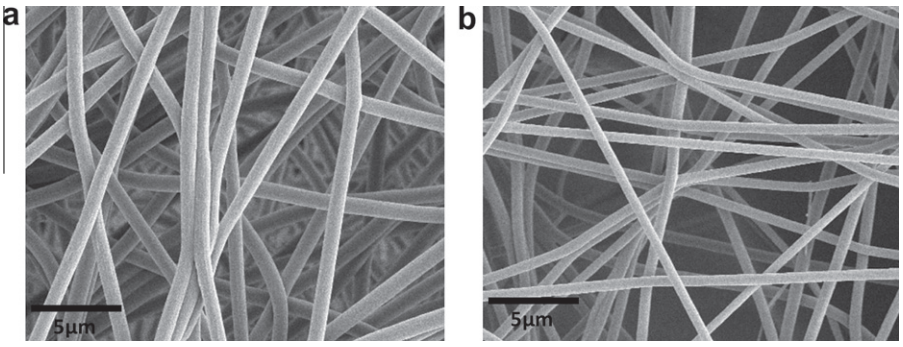

Fig. 4. SEM images of Ag/PAN hybrid nanofibers prepared from plasma-treated $AgNO_3$/PAN solutions. $AgNO_3$ concentration: (a) 0.5%, and (b) 1.25%.

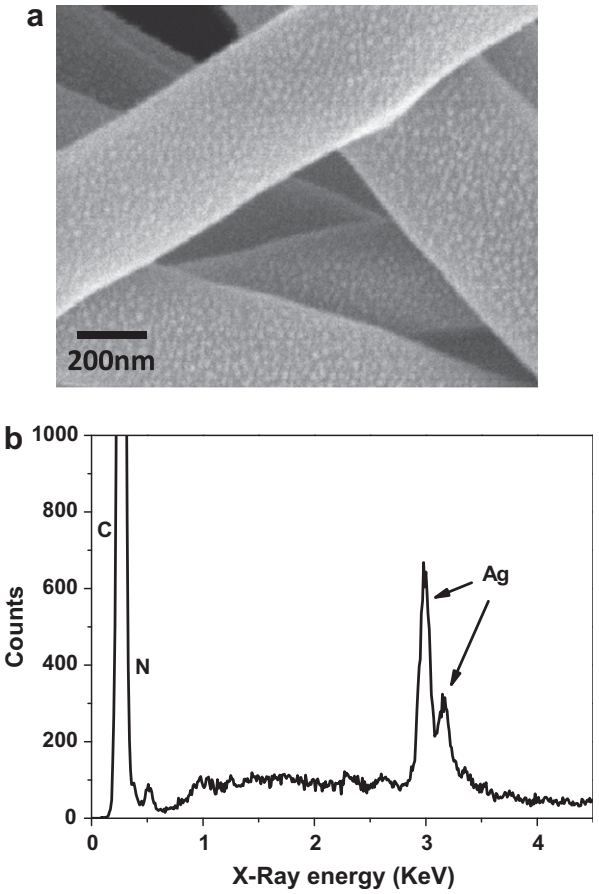

Fig. 5. (a) High-magnification SEM image, and (b) EDX spectrum of Ag/PAN hybrid nanofibers prepared from plasma-treated $AgNO_3$/PAN solution. $AgNO_3$ concentration: 1.25%.

of silver ions. The released silver ions were detected by AAS spectra. Fig. 7 shows the silver release profiles of Ag/PAN hybrid nanofibers over 10 days. The release rate (i.e., the slope of the curve) is relatively high in the first few days and then decreases and levels off after 6 days. The Ag nanoparticles on the surface of nanofibers are readily available to react with water. After the initial release of surface silver, the release process transitions to a diffusion-based release from nanoparticles embedded inside the nanofiber matrix. The cumulative release over 10 days for the $AgNO_3$ concentrations of 0.5% and 1.25% was approximately 45 and 70 ppm, respectively, The silver release rate and cumulative release amount indicate that Ag/PAN nanofibers prepared by plasma pre-treatment can release sufficient silver to exhibit sustained antibacterial activity.

3.4. Antibacterial activity

Antibacterial properties of Ag/PAN nanofibers were tested on both Gram-positive *B. cereus* (Table 2) and Gram-negative *E. coli* (Table 3) microorganisms. For comparison, results for pure PAN nanofibers are also shown. The positive control had 1×10^7 colony forming units (CFU)/ml. Results are expressed as the logarithmic decrease (log reduction) of CFU/ml as compared with the control. As seen in Tables 2 and 3, PAN nanofibers without silver or silver compounds showed no significant antibacterial activity. Conversely, Ag/PAN hybrid nanofibers showed complete inhibition of both Gram-negative and Gram-positive microorganisms, indicating that the nanofibers are endowed with excellent antibacterial properties due to the introduction of Ag nanoparticles. Photographs of agar plates plated with the control cell suspension and those exposed to Ag/PAN hybrid nanofibers (prepared from plasma-treated 1.25% $AgNO_3$/PAN solution) are shown in Figs. 8 and 9, respectively, for Gram-positive and Gram-negative microorganism tests. The absence of

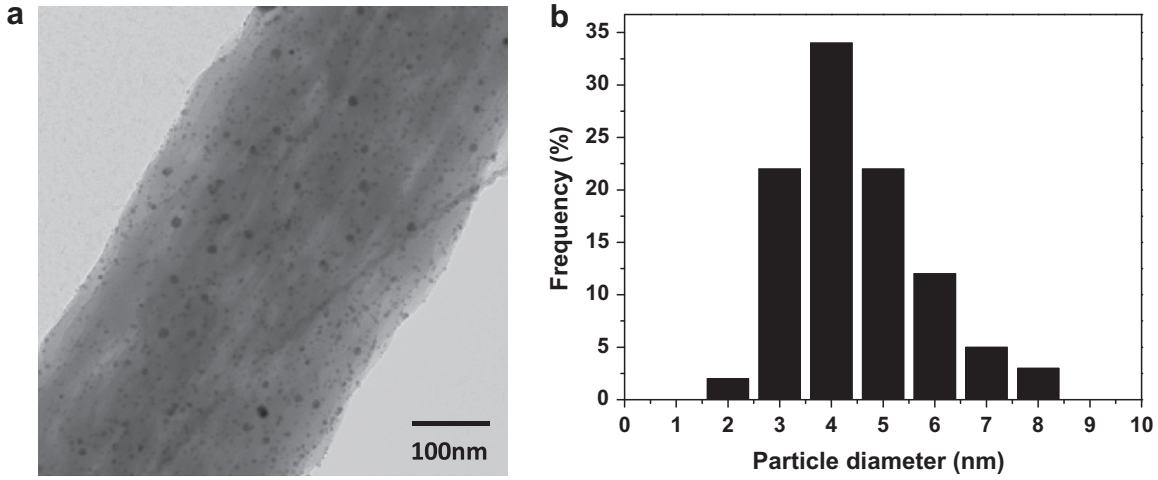

Fig. 6. (a) TEM image, and (b) size distribution of silver nanoparticles in Ag/PAN nanofibers prepared from plasma-treated $AgNO_3$/PAN solution. $AgNO_3$ concentration: 1.25%.

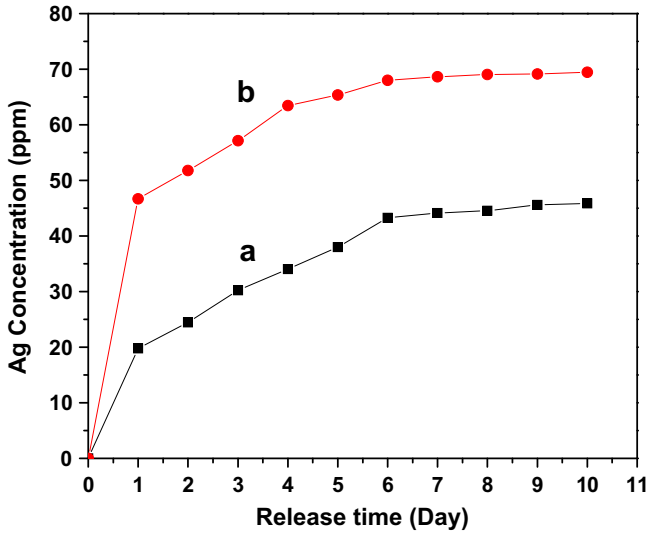

Fig. 7. Silver ion release behaviors of Ag/PAN nanofibers prepared from plasma-treated $AgNO_3$/PAN solutions. $AgNO_3$ concentration: (a) 0.5%, and (b) 1.25%.

Table 2
Antibacterial test results of nanofibers on Gram (+) (*B. cereus*) microorganism.

	Organism only	Pure PAN nanofibers	Ag/PAN nanofibers from plasma-treated 0.5% $AgNO_3$/PAN solution	Ag/PAN nanofibers from plasma-treated 1.25% $AgNO_3$/PAN solution	Ag/PAN nanofibers from plasma-treated 1.25% $AgNO_3$/PAN solution, after 7-day release	$AgNO_3$/PAN nanofibers from untreated 1.25% $AgNO_3$/PAN solution, after 7-day release
Log (CFU/ml)	6.59	6.52	0.00	0.00	0.00	5.46
Log reduction	0.00	0.07	6.59	6.59	6.59	1.13

Table 3
Antibacterial test results of nanofibers on Gram (−) (*E. coli*) microorganism.

	Organism only	Pure PAN nanofibers	Ag/PAN nanofibers from plasma-treated 0.5% $AgNO_3$/PAN solution	Ag/PAN nanofibers from plasma-treated 1.25% $AgNO_3$/PAN solution	Ag/PAN nanofibers from plasma-treated 1.25% $AgNO_3$/PAN solution, after 7-day release	$AgNO_3$/PAN nanofibers from untreated 1.25% $AgNO_3$/PAN solution, after 7-day release
Log(CFU/ml)	6.67	6.31	0.00	0.00	0.00	5.08
Log reduction	0.00	0.36	6.67	6.67	6.67	1.59

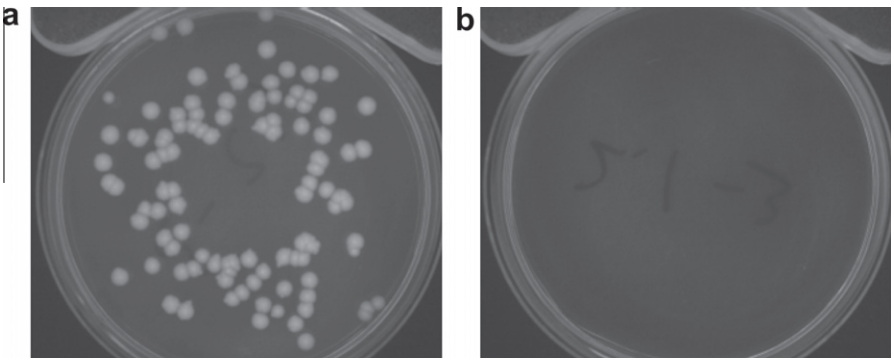

Fig. 8. Antibacterial test plates of *B. cereus* (a) before, and (b) after treatment with Ag/PAN nanofibers prepared from plasma-treated $AgNO_3$/PAN solution. $AgNO_3$ concentration: 1.25%.

colony-forming units on the plates exposed to Ag/PAN hybrid nanofibers suggests a complete kill.

The antibacterial activities of nanofibers electrospun from both plasma-treated and un-treated 1.25% $AgNO_3$/PAN solutions were compared (Tables 2 and 3). After 7 days of release in aqueous solution, the nanofibers electrospun from plasma-treated solution (i.e., Ag/PAN nanofibers) maintained a high level of antibacterial effectiveness. However, in the case of nanofibers electrospun from untreated solution (i.e., $AgNO_3$/PAN nanofibers), only slight antibacterial activity can be observed after 7 days of release in aqueous solution.

TEM images of the inner structures of nanofibers (from plasma-treated and un-treated $AgNO_3$/PAN solutions) after 7 days in deionized water are shown in Fig. 10. For $AgNO_3$/PAN nanofibers electrospun from untreated solution, the water-soluble $AgNO_3$ is released quickly (Fig. 10a) and the antibacterial activity does not last for 7 days (Tables 2 and 3). For Ag/PAN nanofibers electrospun from the plasma-treated solution, Ag nanoparticles are still visible in the nanofiber matrix after 7 days in water (Fig. 10b) and the antibacterial activity is still high. TEM analysis and results from antibacterial test confirm that the durable antibacterial properties of Ag/PAN nanofibers electrospun from the plasma-treated solution are due to the reduction of the $AgNO_3$ to metallic silver, and not simply due to the diffusion of silver ions from the salt.

4. Conclusion

Atmospheric plasma was shown to be a quick and effective method to reduce silver salt into Ag nanoparticles, within 5 min, in a polymer solution without the addition of adverse chemicals. Antibacterial electrospun Ag/PAN nanofibers were successfully prepared by electrospinning plasma-treated $AgNO_3$/PAN solutions. SEM, EDX and TEM images demonstrated the formation of Ag nanoparticles and their uniform dispersion in the nanofiber matrix. The resultant Ag/PAN nanofibers showed excellent antibacterial activity against both Gram-positive and Gram-negative microorganisms. These nanofibers also exhibited good durability in antibacterial activities. After 7 days of release in aqueous solution, the nanofibers prepared from plasma-treated solution still retained strong antibacterial activity. The antibacterial nanofibers have potential applications including implant scaffolds, chemi-

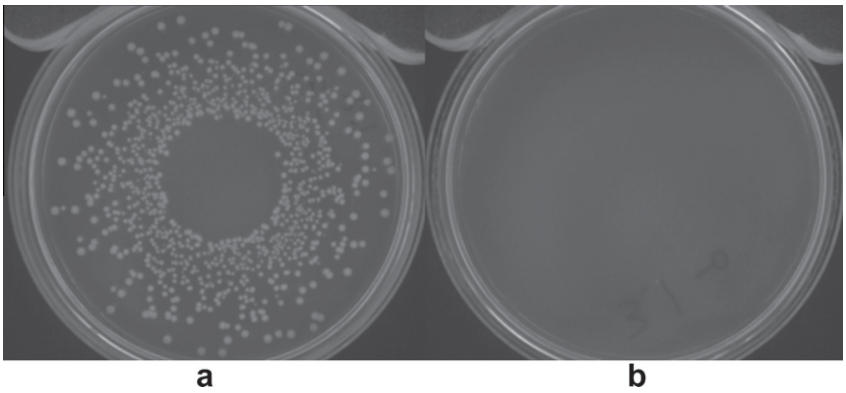

Fig. 9. Antibacterial test plates of *E. coli* (a) before, and (b) after treatment with Ag/PAN nanofibers prepared from plasma-treated $AgNO_3$/PAN solution. $AgNO_3$ concentration: 1.25%.

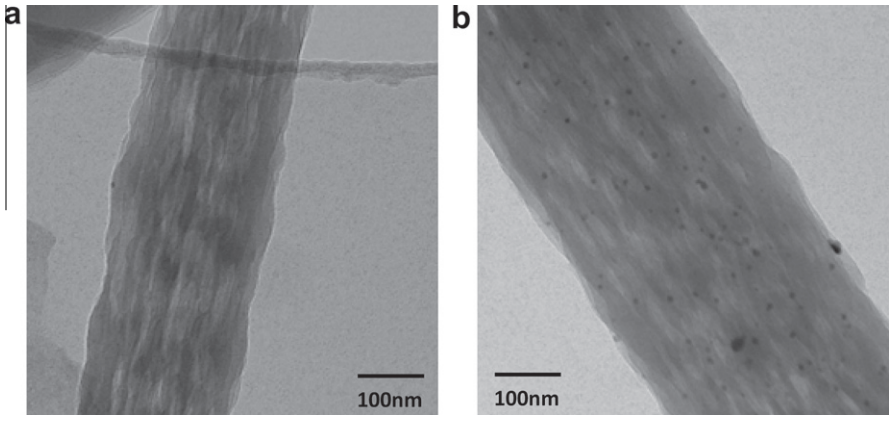

Fig. 10. TEM images of (a) $AgNO_3$/PAN nanofibers prepared from untreated $AgNO_3$/PAN solution, and (b) Ag/PAN nanofibers prepared from plasma-treated $AgNO_3$/PAN solution. $AgNO_3$ concentration: 1.25%.

cal and biological protection, medical devices, and biotextiles.

Acknowledgement

The research work was supported by Defense Threat Reduction Agency (Award No. BB08PRO008).

References

[1] Xu X, Yang Q, Wang Y, Yu H, Chen X, Jing X. Biodegradable electrospun poly(ι-lactide) fibers containing antibacterial silver nanoparticles. Eur Polym J 2006;42(9):2081–7.
[2] Kim SJ, Nam YS, Rhee DM, Park HS, Park WH. Preparation and characterization of antimicrobial polycarbonate nanofibrous membrane. Eur Polym J 2007;43(8):3146–52.
[3] Reneker D, Yarin A. Electrospinning jets and polymer nanofibers. Polymer 2008;49(10):2387–425.
[4] Li D, Xia Y. Electrospinning of nanofibers: reinventing the wheel? Adv Mater 2004;16(14):1151–70.
[5] Kotek R. Recent advances in polymer fibers. Polym Rev 2008;48(2):221–9.
[6] Rutledge G, Fridrikh S. Formation of fibers by electrospinning. Adv Drug Deliv Rev 2007;59(14):1384–91.
[7] Greiner A, Wendorff J. Electrospinning: a fascinating method for the preparation of ultrathin fibers. Angew Chem Int Ed 2007;46(30):5670–703.
[8] Berger T, Spadaro J, Chapin S, Becker R. Electrically generated silver ions: quantitative effects on bacterial and mammalian cells. Antimicrob Agents Chemother 1976;9(2):357–8.
[9] Oloffs A, Grosse-Siestrup C, Bisson S, Rinck M, Rudolph R, Gross U. Biocompatibility of silver-coated polyurethane catheters and silvercoated Dacron® material. Biomaterials 1994;15(10):753–8.
[10] Rai M, Yadav A, Gade A. Silver nanoparticles as a new generation of antimicrobials. Biotechnol Adv 2009;27(1):76–83.
[11] Kim J, Kuk E, Yu K, Kim J, Park S, Lee H, et al. Antimicrobial effects of silver nanoparticles. Nanomed Nanotechnol 2007;3(1):95–101.
[12] Siddhartha S et al. Characterization of enhanced antibacterial effects of novel silver nanoparticles. Nanotechnology 2007;18(22):225103.
[13] Rujitanaroj P-O, Pimpha N, Supaphol P. Wound-dressing materials with antibacterial activity from electrospun gelatin fiber mats containing silver nanoparticles. Polymer 2008;49(21):4723–32.
[14] Xing Z-C, Chae W-P, Baek J-Y, Choi M-J, Jung Y, Kang I-K. In vitro assessment of antibacterial activity and cytocompatibility of silver-containing PHBV nanofibrous scaffolds for tissue engineering. Biomacromolecules 2010;11(5):1248–53.
[15] Wu KH, Yu PY, Hsieh YJ, Yang CC, Wang GP. Preparation and characterization of silver-modified poly(vinyl alcohol)/polyethyleneimine hybrids as a chemical and biological protective material. Polym Degrad Stabil 2009;94(12):2170–7.
[16] Furno F, Morley KS, Wong B, Sharp BL, Arnold PL, Howdle SM, et al. Silver nanoparticles and polymeric medical devices: a new approach to prevention of infection? J Antimicrob Chemother 2004;54(6):1019–24.
[17] Yuan G, Cranston R. Recent advances in antimicrobial treatments of textiles. Text Res J 2008;78(1):60–72.
[18] Pim-on R, Nuttaporn P, Pitt S. Preparation, characterization, and antibacterial properties of electrospun polyacrylonitrile fibrous membranes containing silver nanoparticles. J Appl Polym Sci 2010;116(4):1967–76.
[19] Sichani GN, Morshed M, Amirnasr M, Abedi D. *In situ* preparation, electrospinning, and characterization of polyacrylonitrile nanofibers containing silver nanoparticles. J Appl Polym Sci 2010;116(2):1021–9.
[20] Castellano J, Shafii S, Ko F, Donate G, Wright T, Mannari R, et al. Comparative evaluation of silver-containing antimicrobial dressings and drugs. Int Wound J 2007;4(2):114–22.
[21] Park S, Bae H, Xing Z, Kwon O, Huh M, Kang I. Preparation and properties of silver-containing nylon 6 nanofibers formed by electrospinning. J Appl Polym Sci 2009;112(4):2320–6.
[22] Yeo SY, Lee HJ, Jeong SH. Preparation of nanocomposite fibers for permanent antibacterial effect. J Mater Sci 2003;38(10):2143–7.
[23] Jeon H, Kim J, Kim T, Kim J, Yu W, Youk J. Preparation of poly(ε-caprolactone)-based polyurethane nanofibers containing silver nanoparticles. Appl Surf Sci 2008;254(18):5886–90.
[24] Shin H, Yang H, Kim S, Lee M. Mechanism of growth of colloidal silver nanoparticles stabilized by polyvinyl pyrrolidone in [γ]-irradiated silver nitrate solution. J Colloid Interface Sci 2004;274(1):89–94.
[25] de Santa Maria L, Santos A, Oliveira P, Barud H, Messaddeq Y, Ribeiro S. Synthesis and characterization of silver nanoparticles impregnated into bacterial cellulose. Mater Lett 2009;63(9–10):797–9.
[26] Luong N, Lee Y, Nam J. Highly-loaded silver nanoparticles in ultrafine cellulose acetate nanofibrillar aerogel. Eur Polym J 2008;44(10):3116–21.
[27] Dong X, Ji X, Wu H, Zhao L, Li J, Yang W. Shape control of silver nanoparticles by stepwise citrate reduction. J Phys Chem C 2009;113(16):6573–6.
[28] Kumar A, Chhatra R, Pandey P. Synthesis of click bile acid polymers and their application in stabilization of silver nanoparticles showing iodide sensing property. Org Lett 2010;12(1):24–7.
[29] Sharma V, Yngard R, Lin Y. Silver nanoparticles: green synthesis and their antimicrobial activities. Adv Colloid Interface 2009;145(1–2):83–96.
[30] Raveendran P, Fu J, Wallen S. A simple and "green" method for the synthesis of Au, Ag, and Au–Ag alloy nanoparticles. Green Chem 2006;8(1):34–8.
[31] Hu B, Wang S, Wang K, Zhang M, Yu S. Microwave-assisted rapid facile "Green" synthesis of uniform silver nanoparticles: self-assembly into multilayered films and their optical properties. J Phys Chem C 2008;112(30):11169–74.
[32] Li S, Shen Y, Xie A, Yu X, Qiu L, Zhang L, et al. Green synthesis of silver nanoparticles using *Capsicum annuum* L. extract. Green Chem 2007;9(8):852–8.
[33] Lee H, Jeong E, Baek C, Youk J. One-step preparation of ultrafine poly (acrylonitrile) fibers containing silver nanoparticles. Mater Lett 2005;59(23):2977–80.
[34] Krutyakov Y, Kudrinskiy A, Olenin A, Lisichkin G. Synthesis and properties of silver nanoparticles: advances and prospects. Russ Chem Rev 2008;77(3):233–57.
[35] Huang H, Yang X. Synthesis of polysaccharide-stabilized gold and silver nanoparticles: a green method. Carbohydr Res 2004;339(15):2627–31.
[36] Tendero C, Tixier C, Tristant P, Desmaison J, Leprince P. Atmospheric pressure plasmas: a review. Spectrochim Acta B 2006;61(1):2–30.
[37] Laroussi M, Akan T. Arc-free atmospheric pressure cold plasma jets: a review. Plasma Processes Polym 2007;4(9):777–88.
[38] Van Durme J, Dewulf J, Leys C, Van Langenhove H. Combining non-thermal plasma with heterogeneous catalysis in waste gas treatment: a review. Appl Catal B – Environ 2008;78(3–4):324–33.
[39] Fridman A. Plasma chemistry. Cambridge Univ. Press; 2008.
[40] Richmonds C, Sankaran R. Plasma-liquid electrochemistry: rapid synthesis of colloidal metal nanoparticles by microplasma reduction of aqueous cations. Appl Phys Lett 2008;93:131501.
[41] Sato T, Miyahara T, Doi A, Ochiai S, Urayama T, Nakatani T. Sterilization mechanism for *Escherichia coli* by plasma flow at atmospheric pressure. Appl Phys Lett 2006;89:073902.
[42] Stoffels E, Sakiyama Y, Graves D. Cold atmospheric plasma: charged species and their interactions with cells and tissues. IEEE Trans Plasma Sci 2008;36(4):1441–57.
[43] Matthews S, McCord M, Bourham M. Poly (vinyl alcohol) desizing mechanism via atmospheric pressure plasma exposure. Plasma Processes Polym 2005;2:702–8.
[44] Matthews S, Hwang Y, McCord M, Bourham M. Investigation into etching mechanism of polyethylene terephthalate (PET) films treated in helium and oxygenated-helium atmospheric plasmas. J Appl Polym Sci 2004;94:2383–9.
[45] McCord M, Hwang Y, Qiu Y, Hughes L, Bourham M. Surface analysis of cotton fabrics fluorinated in radio frequency plasma. J Appl Polym Sci 2003;88:2038–47.
[46] Carl DS, Joshua LM, Saad AK. Electrospun nanoparticle–nanofiber composites via a one-step synthesis. Small 2009;5(8):944–51.
[47] Jin W-J, Lee HK, Jeong EH, Park WH, Youk JH. Preparation of polymer nanofibers containing silver nanoparticles by using poly(*N*-vinylpyrrolidone). Macromol Rapid Commun 2005;26(24):1903–7.
[48] Lin Z, Ji L, Zhang X. Electrocatalytic properties of Pt/carbon composite nanofibers. Electrochim Acta 2009;54(27):7042–7.
[49] Kumar R, Munstedt H. Silver ion release from antimicrobial polyamide/silver composites. Biomaterials 2005;26(14):2081–8.