Materials Science and Engineering C 70 (2017) 1011–1017

Contents lists available at ScienceDirect

Materials Science and Engineering C

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

Fabrication of silver nanowires-loaded polydimethylsiloxane film with antimicrobial activities and cell compatibility

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ARTICLE INFO

Article history:
Received 29 January 2016
Received in revised form 27 March 2016
Accepted 28 April 2016
Available online 29 April 2016

Keywords:
Silver nanowires
PDMS film
Antimicrobial
Antibacterial and cell compatibility

ABSTRACT

Microbial contamination on various surfaces is one of the greatest health problems worldwide, afflicting millions of peoples annually. Given the advantages of silver nanowires (AgNWs) in forming a percolated network when fabricated into a film, there is significant interest in developing AgNWs loaded polymeric coatings for antimicrobial applications. In this work, AgNWs with high aspect ratio are drop-coated onto a silicon wafer to form a uniform interconnected network. The AgNW network is then embedded into polydimethylsiloxane (PDMS) matrix to fabricate AgNWs/PDMS film. The PDMS loaded with various amounts of AgNWs can efficiently destroy *Escherichia coli* and *Staphylococcus aureus* bacteria, and PDMS with 0.2 mg of AgNW loading (i.e. 50 μg cm^{-2}) exhibit excellent cell compatibility. Furthermore, AgNWs/PDMS films show a long-term antibacterial effect for at least one month. The utilization of AgNWs in polymeric coatings provides a novel platform to reduce the microorganism infection.

1. Introduction

Microbial surface contamination has become widespread and is of serious concern globally due to the significant risk of pathogen transmission from contaminated surfaces to human [1,2]. Generally, microorganisms adhere and start multiplying rapidly on surfaces (e.g. medical devices, wound dressing, food packages, separation membranes) when subjected to suitable environmental conditions. Moreover, the persistent nature of microorganisms makes it difficult for their complete removal. There is a demand to solve this pressing problem. One efficient strategy is through the utilization of bioactive surface coating that releases antimicrobial materials to destroy adherent and surrounding microorganisms, resulting in the reduction of infection [3–7].

As a broad-spectrum antimicrobial material, silver has been widely utilized in healthcare [8,9]. In ancient times, silver was used for treatment of burnt skin to stimulate wound healing. Today, silver has been proposed in several products including medical devices (e.g. dental amalgams, catheters), topical cream in the treatment of burn wounds, and filter membranes in water system [5,10,11]. These broad applications of silver stem from its efficient antimicrobial activity and low toxicity to human cells. The use of silver in its different forms (metal, salt, nanomaterials) was discussed in many literatures. For example, silver metal can be electrolytically deposited on medical instruments as implant devices [12]. It can continuously release small amount of silver ions, which act antimicrobially at the metal surface. However, the antimicrobial application of silver metal requires the oxidation to silver ions, which is a slow process that may lead to low efficiency. Therefore, silver salts were directly introduced into the surface coatings, leading to a reasonable local silver concentration and efficient antimicrobial effect. Silver salts with different solubility (e. g. high soluble silver nitrate, sparingly soluble silver halides and silver sulfide, insoluble silver phosphate) were incorporated into various devices to control the release of silver ions, thus achieving ideal antimicrobial effects [8,13]. In order to develop long-term solution for better success in controlling microorganism infections, the currently available nanotechnology tools are required. Nanosilver exhibits excellent antimicrobial properties due to their high surface-to-volume ratio and specific physiochemical characteristics that are different from bulk silver [14]. Nanosilver elicits antibacterial effects mainly due to the aerobic release of silver ions [9,14]. Polymeric materials, with great structure tailorability and flexibility, have immense potential as an antimicrobial coating through incorporating nanosilver to achieve long-term silver ions release and inhibit nanosilver aggregation [15].

Polydimethylsiloxane (PDMS) is a promising polymer as a coating due to its high flexibility, low surface energy, low cost, good biocompatibility, chemical inertness and transparency [16]. To confer bactericidal activities to PDMS, silver nanoparticles were incorporated in PDMS to form an advanced antimicrobial coating [17–19]. For example, zinc oxide nanorod array was fabricated on PDMS, followed by an in situ deposition of silver nanoparticles through a photoreduction process [18]. Another nanocomposite was based on the dispersion of silver

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http://dx.doi.org/10.1016/j.msec.2016.04.094
0928-4931/

nanoparticles (0.25 wt%) within PDMS [17]. Both systems exhibited evident antimicrobial efficiency, however, there are concerns about the uncontrollable release of silver nanoparticles (deposited on the coating surface) into the environment and the limited release rate of silver ions from the silver nanoparticles (dispersed in the matrix). In comparison to silver nanoparticles, the highly anisotropic silver nanowires have the advantages in forming a percolated network when fabricated as a film or applied to a matrix [20]. The interconnected nanowires film in a matrix will allow continuous release of silver ions after the nanowires corrosion [21]. Moreover, silver nanowires are known to be safe for humans and widely used in flexible electronics [22,23]. Therefore, the antimicrobial effects and cell compatibility of silver nanowires loaded in PDMS film were investigated in this paper.

Silver nanowires (AgNWs) with a high aspect ratio were synthesized via the polyol reduction of silver nitrate ($AgNO_3$). A uniform network of interconnected AgNWs was fabricated on a silicon wafer by using a drop-coating method. The AgNW film on silicon wafer was further loaded into PDMS matrix to control the release of silver ions and destroy the bacteria through the contact killing. The antibacterial assay of PDMS loaded with AgNWs at different amounts was performed against gram-negative bacteria *Escherichia coli* (*E. coli*) and gram-positive bacteria *Staphylococcus aureus* (*S. aureus*). The morphology and cytoskeletal architecture of human dermal fibroblasts adhered on the AgNWs/PDMS films were examined. The optimal loading amount of AgNWs with high antibacterial effect and low cytotoxicity was determined. The AgNWs loaded PDMS film also successfully exhibit a long-term antibacterial effect for at least one month. The use of AgNWs in polymeric coatings may open a new opportunity to reduce the microorganisms infection.

2. Materials and methods

2.1. Materials

$AgNO_3$ (99%), poly-(vinylpyrrolidone) (PVP) powder (avg Mw ~ 55,000), $CuCl_2 \cdot 2H_2O$ (99.9%), NaCl (99%) and ethylene glycol (99.8%) were purchased from Sigma-Aldrich and used without further purification. 1H,1H,2H,2H-perfluorododecyltrichlorosilane (FDTS) was purchased from Alfa Aesar. Silicon wafer (Prime silicon wafer 6″, thickness 625 ± 25 μm, single side polished) was purchased from Latech Scientific Supply Pte. Ltd. and cut into 20 × 20 mm slides. Sylgard® 184 PDMS elastomer kit including PDMS precursor and PDMS curing agent was purchased from Best Chemical Co(s) Pte Ltd. Live/dead® Baclight™ bacteria viability kit including SYTO 9 and propidium iodide was purchased from Life Technologies Corporation. Deionized (DI) water was used throughout all the experiment.

2.2. Synthesis of AgNWs

AgNWs were synthesized by reducing $AgNO_3$ in ethylene glycol in the presence of PVP. In a typical synthesis, 5 mL of pure ethylene glycol was added to a glass vial which was suspended in an oil bath (temperature at 150 °C) for 1 h under magnetic stirring at 260 rpm. After that, 40 μL of a 4 mM $CuCl_2$ solution in ethylene glycol was added in and heated for another 15 min, followed by the dropwise injection of 1.5 mL of 0.15 M PVP solution in ethylene glycol and 1.5 mL of 0.1 M $AgNO_3$ solution in ethylene glycol. After 1 h, the reaction was stopped by cooling the reaction vial in room temperature. AgNW solution was obtained by washing with acetone (40 mL) once and DI water (40 mL) three times via redispersion-centrifugation (2000 rpm, 20 min). The purified AgNWs were dispersed in water for further uses.

2.3. Fabrication of AgNWs/PDMS films

Silicon wafer (20 × 20 mm) was cleaned with ultrasonication in acetone and isopropanol solution for 10 min respectively and followed by oxygen plasma for 3 min at 250 W power. The as-cleaned wafer was coated with FDTS using a vapor deposition method. 1 mL of AgNW solution in water at 1, 0.5 or 0.2 mg/mL was carefully dropped on the surface of FDTS-coated silicon wafer and heated to evaporate water at 100 °C in the Binder oven. After 1 h, a thin AgNW network containing 1, 0.5 or 0.2 mg AgNWs was uniformly formed on the silicon substrate. Subsequently, 4.5 mL of PDMS precursor was mixed with 0.45 mL of PDMS

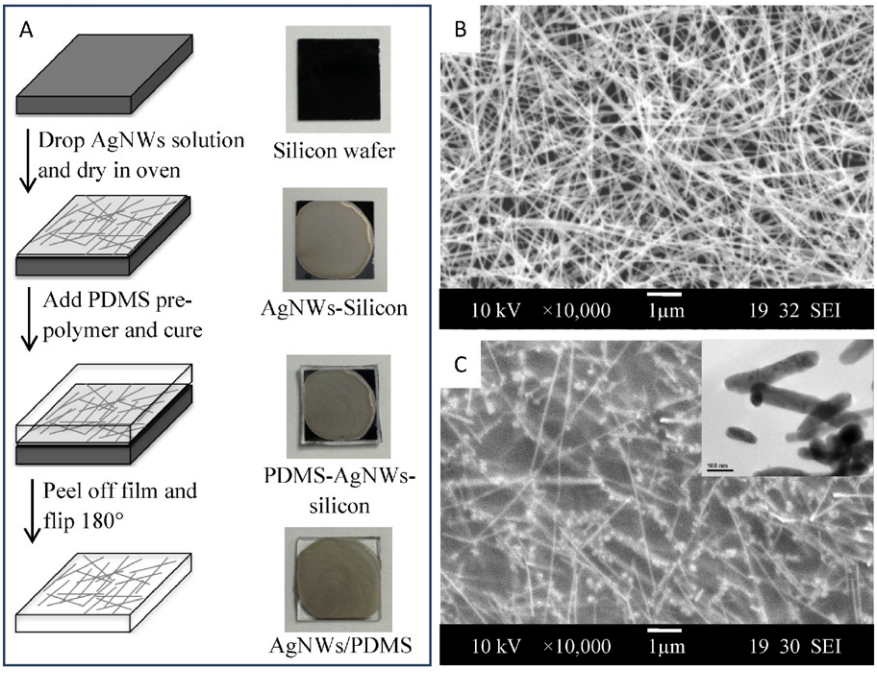

Fig. 1. Fabrication and characterization of AgNWs/PDMS film. (A) Schematic illustration and photographs of the fabrication process of AgNWs/PDMS film. (B) SEM image of AgNWs network on the surface of silicon wafer. Scale Bar = 1 μm. (C) SEM image of the peeled AgNWs/PDMS film at the surface facing to silicon wafer. Scale Bar = 1 μm. Insert is TEM image under low magnification (Scale Bar = 100 nm).