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Facile fabrication of silver-nanowire-based chips using dry-film photoresist for wearable optical detection

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Abstract

With technological advances in wearable health care monitoring system, there increasing demands for the patterning technology for reliable sensors. Dry-film photoresists (DFRs) have several advantages for the patterning of silver nanowires (AgNWs), including cost-effectiveness, low toxicity of the process, and ease of mass production through a roll-to-roll process. In this study, using DFRs, we achieved the facile fabrication of AgNW-based chips for optical detection of myoglobin (Mb) via surface-enhanced Raman spectroscopy (SERS). Mb is found in accessible biological fluids such as urine and serum, which is a representative protein biomarker for human health monitoring. AgNWs were successfully patterned on polyethylene terephthalate films using DFR to form multiple spots, with a diameter of ~500 μm, that are available for detection. SERS spectra showed that the AgNW chips can efficiently detect myoglobin proteins down to levels of clinical significance. Our results will provide insights for the cost-effective production method of futuristic health care monitoring system.

Keywords: Silver nanowires, Patterning, Dry film photoresist, Sensor, Surface-enhanced Raman scattering

Introduction

The increasing adoption of point-of-care technologies as well as of rapid and cost-effective monitoring systems that can provide information on the progression of diseases and suggest therapeutic strategies on demand is rapidly revolutionizing the healthcare field (Iqbal et al., 2021; Kamei et al., 2015; Li et al., 2020; Miller et al., 2007; Sharma et al., 2017; Uddin, 2019). However, some technical requirements, including low production costs, simple and rapid detection, sufficient sensitivity, and non-invasiveness, impede the practical applicability and commercialization of such systems. In this context, novel advanced materials and nanotechnologies are anticipated to be the key drivers of next-generation sensing.

Nanowire networks comprising noble metals are promising materials for integration with optical chips owing to their large surface area, easy manipulation, stability in harsh physiological environments, and simple and scalable fabrication processes (Barucci et al., 2021; De et al., 2009; Groep et al., 2012). Thus far, many reports have discussed the

potential of nanoscale metallic devices in healthcare (Chang et al., 2020; Ramirez et al., 2020); however, there are limited works on metal-nanowire-based healthcare systems.

Metal-nanowire-based networks, especially those intended for integration with low-cost sensing devices, are typically patterned in the micrometer scale once they are supported on a plastic substrate, conferring sensing systems with high sensitivity, reproducibility, and effectiveness (Amjadi et al., 2014; Gong et al., 2015; Kim et al., 2015, 2018). Conventional lithography using liquid photoresists (PRs) has limited applicability for stretchable electronics because the uniform control of the thickness of liquid PRs and pattern size on polymeric substrates is difficult; moreover, the necessity of a post-thermal annealing process to evaporate the solvent could damage the substrate and increase the processing costs (Schober et al., 2020; Wu et al., 2010). Furthermore, an organic-based, toxic developer is used for liquid-PR-based patterning, which could degrade soft polymer substrates (Mooney et al., 2020; Wang et al., 2013).

Solid-state dry-film photoresists (DFRs) can be deposited using a simple lamination process; thus, simple, fast, and cost-effective patterning is possible. Moreover, this process is directly applicable to the roll-to-roll manufacturing scheme required for the mass production of large-scale flexible devices (Kim & Hwang, 2018; Stephan et al., 2007; Tsai et al., 2006). DFR patterning uses non-toxic chemicals (Kim et al., 2017), and an additional investment is not required to replace the conventional patterning procedure because the remaining steps for patterning, except the lamination, are the same as those used in the conventional patterning process using liquid PRs (Nilsen et al., 2019; Stephan et al., 2007).

In this study, a DFR-based patterning technology was developed for the fabrication of metal-nanowire-based chips to overcome the limitations of liquid-PR-based patterning processes. AgNW networks were successfully patterned on PET using a DFR to achieve multiple spots, thereby forming low-cost chips for the optical sensing of myoglobin (Mb), which was chosen in this study as a representative protein biomarker of several health impairments. Mb is found in accessible biological fluids such as urine and serum (Aydin et al., 2019; Premru et al., 2013; Yu et al., 2021). The detection efficiency of the implemented AgNW-based chips was investigated by surface-enhanced Raman scattering (SERS), which has recently emerged as a powerful optical tool for obtaining chemical and structural information from trace biomolecules in body fluids and physiological environments (Amicucci et al., 2021; Banchelli et al., 2019).

Methods

A 0.5 wt% AgNW suspension in ethanol was purchased from Nanopyxis and used without post-treatment. The average diameter and length of the AgNWs were ~ 35 nm and 25 μm, respectively. The AgNWs were coated on a PET substrate (KOLON Industries) with a thickness of 125 μm by using a Meyer bar (RD Specialties Inc., #6). The initial sheet resistance of the deposited AgNW electrodes was 3.4 ± 0.6 Ω/sq. The less densities of AgNWs than the condition of the initial sheet resistance resulted in the less SERS signal, which is not preferable for the sweat sensor. Thus, the density optimized to have the initial sheet resistance of 3.4 ± 0.6 Ω/sq was the optimized condition in consideration of costs and sensing performance. A DFR (KOLON Industries, KL-1015), with dimensions of 50 m (total length) × 15 μm (thickness) × 30 cm (width), was laminated on the AgNW

electrode on the PET substrate using a laminator (Jaesung Engineering, JSL-1200) at 80 °C, a rolling speed of 1.6 m/min, and a roll gap of 1 mm. UV exposure for patterning was conducted through a film combine glass (FCG) mask in a vacuum. Na_2CO_3 (1 wt%, Sigma-Aldrich) and NaOH (4 wt%, Sigma-Aldrich) solutions were used for developing and stripping, respectively. The microstructure of the patterned AgNW networks was characterized by optical microscopy (OM, Olympus, BX51) and scanning electron microscopy (SEM, Phillips, XL30 ESEM–FEG). The morphology of the samples under prolonged immersion in a protein solution was investigated by atomic force microscopy (AFM, Bruker). SERS analysis was performed under a micro-Raman spectrometer (XPlora, Horiba) with a 532 nm excitation wavelength, 1200 grooves/mm grating, 10× objective, 135 μW laser power, and 5 s integration time. SERS spectra were obtained by pouring 5 μL of different Mb sample solutions (within the 10^{-5}–10^{-8} M range) onto single spots of the AgNWs/PET chip and allowing the solutions to dry. The SERS data presented herein are an average of 20 spectra collected by mapping experiments over 12 mm^2 areas within the deposited sample.

Results and discussion

A schematic of the fabrication and detection process of the AgNW chip prepared using a DFR is presented in Fig. 1. First, AgNWs were deposited on the PET film using a Mayer rod, followed by a thermal baking process at 150 °C for 20 min. AgNWs were partially embedded on the surface of the PET film by the thermal baking process; thus, stable patterning was possible without the loss of nanowires during the post-development or stripping process. Insufficient thermal baking resulted in a substantial loss of AgNWs during the patterning process owing to their low adhesion toward PET (Additional file 1: Fig. S1a), while AgNWs subjected to excessive thermal baking showed inadequate sensing performance owing to thermal damage (Additional file 1: Fig. S1b). Next, the AgNWs/PET films were coated with the DFR through a simple lamination process, whereby a sticky polymer binder with acrylic acid branches on the surface of the DFR provided sufficient adhesion between the DFR and samples. The patterning process was preceded by exposing the DFR-coated samples to UV light through a FCG photomask. UV exposure

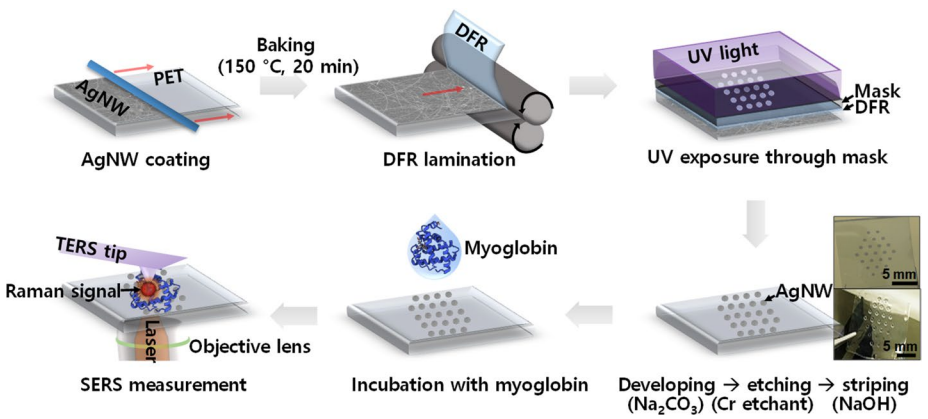

Fig. 1 Schematic of the fabrication and optical detection process of AgNW/PET chips

was conducted for 120 s. Since the DFR is a negative-type photoresist, the area exposed to UV light was cured, bonding strongly with the AgNWs. A circular pattern was chosen because it proves beneficial for effective drop-deposition detection (Banchelli et al., 2019); thus, all the patterns in this study were fixed as spots with a diameter of 500 μm. The portion of the DFR not exposed to UV light was dissolved by an alkaline solution of Na_2CO_3, according to the following chemical reaction (An et al., 2017):

$$Na_2CO_3 \leftrightarrow Na^+ + NaCO_3^-$$

$$NaCO_3^- + H_2O \leftrightarrow NaHCO_3 + OH^-$$

$$DFR - COOH + Na^+ + OH^- \rightarrow DFR - COONa^+ + H_2O.$$

After development, a clear spot with a diameter of ~ 500 μm, corresponding to the cured DFR on the silver nanowires, was observed, as shown in Fig. 2a. Etching was achieved using a typical chrome etchant, whereby only the exposed AgNWs were removed. A stronger alkaline NaOH treatment was then performed to strip the cured DFR, where the chemical reaction between the acrylic acid in the DFR and OH^- eliminated the adhesive characteristics of DFR through the following mechanism (Kim et al., 2011):

$$NaOH \leftrightarrow Na^+ + OH^-$$

$$DFR - COOH + OH^- \rightarrow DFR - COONa^+ + H_2O.$$

A clear spot with sharp edges corresponding to the AgNWs was observed after the stripping process, as shown in Fig. 2b, c. Finally, the AgNW chips were washed for 2 h in acetone to remove organic contaminants and then stored under vacuum at room temperature until the time of characterization and SERS analysis.

The stability of the AgNWs was tested by prolonged incubation of the chip in a 10^{-6} M aqueous solution of Mb (Fig. 3a, b), revealing the absence of significant changes to morphology even after 1 h, which confirmed the reliability of the AgNW chips given their resistance to biochemical solutions. To show the feasibility of the patterned AgNWs chips for optical detection, 5 μL of Mb solutions of decreasing Mb concentrations were

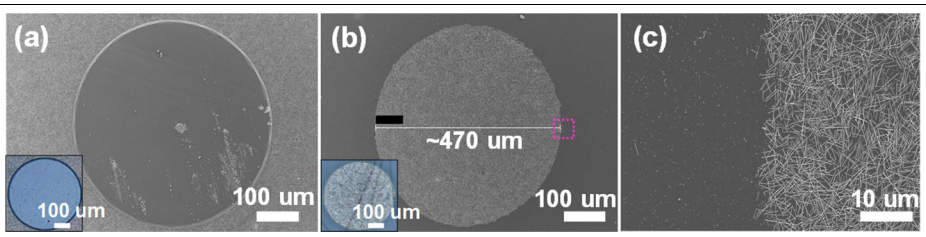

Fig. 2 SEM images of the AgNW spot after the development process (**a**), and etching and stripping (**b**). Enlarged SEM image corresponding to the interface between the AgNWs and the PET substrate (**c**) (magenta square from (**b**)). Insets are OM images taken at the corresponding steps of **a** and **b**

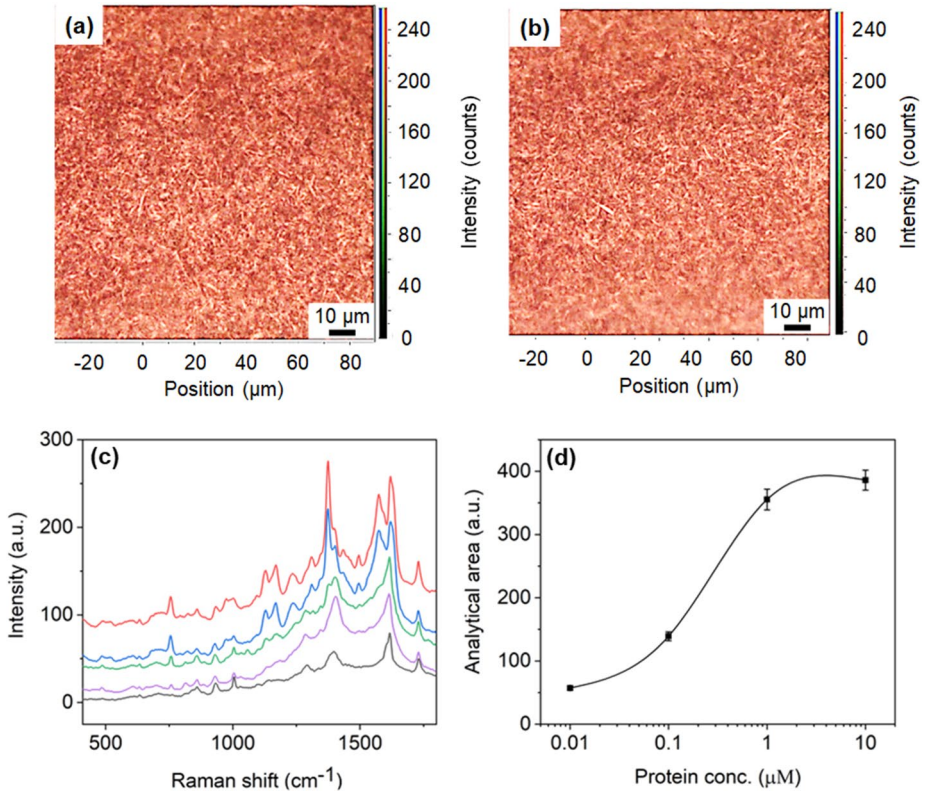

Fig. 3 AFM tomography of AgNWs/PET chips **a** before and **b** after incubation in a Mb aqueous solution. **c**, **d** SERS detection with AgNWs/PET chips. **c** SERS spectra of Mb solutions with concentrations ranging from 10^{-8} M to 10^{-5} M (black, naked chip; violet, 10^{-8} M; green, 10^{-7} M; blue, 10^{-6} M; red, 10^{-5} M). **d** Correlation between the 756 cm^{-1} band area and protein concentration (error bars represent the standard deviation)

dropped on single AgNW spots. After drying at room temperature, an SERS analysis was performed. Figure 3c shows the SERS patterns of the deposited samples under 532 nm laser excitation; notably, characteristic intense peaks that are mainly ascribed to the heme group of Mb (Banchelli et al., 2019) can be observed, such as those at 1623 cm^{-1} (v10), 1580 cm^{-1} (v19), 1440 cm^{-1} (v28), 1375 cm^{-1} (v4), 1229 cm^{-1} (v13), 1170 cm^{-1} (v30), 1134 cm^{-1} (v22), 990 cm^{-1} (v4), and 756 cm^{-1} (v15). A sigmoidal correlation between the band area of the 756 cm^{-1} mode and the protein concentration was observed within the 10^{-8}–10^{-5} M range, and a plateau was observed at high values due to the saturation of all the accessible hotspots of the SERS substrate (Fig. 3d). The lowest detectable value of 10^{-8} M (corresponding to approximately 200 g/L) suggests the possibility of the quantitative detection of Mb in biofluids at levels of diagnostic and prognostic significance for renal and cardiac impairments (Loun et al., 1996).

Conclusions

In this study, a AgNW chip for the optical monitoring of Mb was fabricated by using a DFR. AgNWs were coated on a PET substrate, followed by post-thermal baking at 150 °C for 20 min. A DFR was then laminated on AgNWs/PET, which was subsequently patterned by a photolithography process. Patterning using DFR is a

low-toxicity process because mild alkaline solvents were used during the developing and stripping steps. Through the DFR-based process, AgNWs were successfully patterned to obtain multiple spots with a diameter of ~ 500 μm without significant damage to the patterns. Finally, SERS was employed to confirm the feasibility of the AgNWs/PET chips for the optical detection of Mb. The results showed that protein concentration levels of clinical significance can be easily detected via the combination of the developed AgNWs/PET chips with SERS analysis.

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s40691-022-00297-6.

Additional file 1: Figure S1. Optical microscope images of AgNWs baked at (a) 100 °C for 20 min and at (b) 180 °C for 20 min.

Acknowledgments
Not applicable.

Author contributions
C. Amicucci & H. Ha prepared samples and performed experiments. P. Matteini & B. Hwang designed experiments and analyzed data. C. Amicucci, H. Ha, P. Matteini & B. Hwang drafted manuscript. All authors read and approved the final manuscript.

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Availability of data and materials
The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Competing interests
The authors declare that they have no competing interests.

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