Simple fabrication of Ag nanoparticles impregnated electrospun nanofibers as SERS substrates

Altangerel Amarjargal[1,2,*], Leonard D. Tijing[3], Cheol Sang Kim[1, 4,*]

[1]Department of Bionanosystem Engineering, Chonbuk National University, Jeonju, Jeonbuk 561-756, Korea

[2]Power Engineering School, Mongolian University of Science and Technology, Ulaanbaatar, Mongolia

[3] School of Civil and Environmental Engineering, University of Technology, Sydney (UTS), P.O. Box 123, Broadway, NSW 2007, Australia

[4] Division of Mechanical Design Engineering, Chonbuk National University, Jeonju, Jeonbuk 561-756, Korea

[*]Corresponding authors: C.S. Kim; Tel.: +82-63-270-4284; Fax: +82-63-270-2460; E-mail: chskim@jbnu.ac.kr; and A.Amarjargal; Fax: +82-63-270-2460; E-mail: a_amaraa1@jbnu.ac.kr, a_amaraa1@yahoo.com

Abstract

In this communication, a facile method for the fabrication of electrospun polyurethane (PU) nanofibers impregnated with Ag nanoparticles (NPs) as an efficient and free-standing SERS substrates is reported. Electrospinning was used to produce polymeric nanofibrous matrix, whereas liquid polyol (ethylene glycol) under low temperature was used not only to reduce Ag^+ to Ag^0, but also was employed as the *in situ* growth medium for well-dispersed Ag NPs on the surface of fiber nets. Large enhancement in Raman signals of 4-mercaptobenzoic acid (4-MBA) analytes could be realized in the present Ag/PU nanofibers due to the presence of SERS "hot-spots" by means of appropriate interparticle gap.

1. Introduction

In the last decade, surface-enhanced Raman scattering (SERS) has grown to become powerful analytical tool for ultrasensitive detection of chemical and biological molecules down to the single molecular level, which can be applied in various fields including life science, analytical chemistry, biomedical and environmental science [1-5]. SERS offers tremendous enhancement of the Raman signals by molecules in the presence of a nanostructured metallic surface, especially noble metals such as Ag, Au and Cu nanoparticles (NPs). In general, it is widely accepted that the enhancement effect of SERS usually proceeds via two distinct mechanisms: electromagnetic enhancement that is associated with the localized surface plasmon resonances occurring at the surfaces of roughened metal substrates or metal clusters and chemical enhancement which is associated with the direct charge transfer or indirect electron-hole pair excitation processes [6, 7].

Recent studies have found that the substrates having remarkable SERS activity/sensitivity can be achieved by controlled assembly or deposition of noble metal NPs on/in the one-dimensional (1D) nanostructure due to the presence of Raman "hot-spots" by means of gap distance between particles. When deposited, plasmonic NPs on the support are in close proximity, individual plasmon oscillations can couple with each other, resulting in huge local electromagnetic field enhancements in these confined junctions or this hot-spots [8-10]. For example, Bao et al. [11] fabricated poly(methyl methacrylate) (PMMA) nanofibers in the form of overlaid films, surface decorated with Ag NPs facilitated via oxygen plasma etching, which were explored as active substrates for SERS.

Here, we report a simple and cheap way to mass-produce Ag/PU nanofibers. The aim of the present work was to prepare efficient and free-standing SERS substrates with high enhancement factor by electrospun nanofibers impregnated with Ag NPs through combining the methods of electrospinning and polyol immersion, in the absence of any surfactant or sensitizing and stabilizing reagent. Here, the function of ethylene glycol (EG) solvent under low temperature was not only to reduce Ag^+ to Ag^0, but also employed as the *in situ* growth medium for well-dispersed Ag NPs on the surface of fiber nets.

2. Experimental

Polyurethane (PU, 10 wt.%) solution was prepared by dissolving appropriate amount of PU pellets (Skythane® X595A-11) in *N,N* dimethylformamide (DMF) and methyl ethyl ketone/2-butanone (MEK,) (50/50, wt:wt%, Showa) solvent solution. The solution was electrospun into nanofibers at 11 kV, tip-to-collector distance of 15 cm and solution feed rate of 1 mlh^{-1} [12]. After electrospinning, the PU nanofibrous mat was dried at 80°C for 48 h to remove the residual solvents.

The Ag NPs impregnated electrospun PU nanofibers were performed by polyol immersion technique, which was similar to our previous report [13]. Briefly, electrospun PU nanofibrous were immersed in a previously-prepared EG solution that dissolved 0.05 g $AgNO_3$ and 0.07 g polyvinylpyrolidone (PVP), incubated at 60 °C under soft shaking. Mat samples were taken out after 20 h of immersion, and were then thoroughly rinsed with deionized water and dried at 60 °C for 24 h.

The surface structure and morphology of the present samples powder were studied by field emission scanning electron microscopy (FE-SEM, S-7400, Hitachi, Japan), and the elemental composition was checked using an energy dispersive spectrometer (EDS). X-ray powder diffraction (XRD) analysis was carried out by a Rigaku X-ray diffractometer (Cu Kα, λ = 1.54059 Å). SERS measurements were performed using a Nanofinder 30 Raman confocal spectroscopy device (Tokyo Inst. Co., Japan) equipped with a He:Ne laser (λ = 633 nm). A 50 × microscope objective was used to focus the laser beam to obtain the SERS spectra and the laser power incident on the samples was 2 mW excitation.

3. Results and Discussion

By utilizing a two-step route, the well-distributed assembly of Ag NPs on the electrospun nanofibers was successfully fabricated through a simple and controllable manner. The structure of the Ag/PU composite nanofibers was characterized by XRD and the result is shown in Fig. 1a. The number of well-defined Bragg reflections with 2θ values at 38.2˚, 44.6˚, 64.2˚ and 77.2˚ in the XRD pattern of Ag/PU composite nanofibers can be indexed to (111), (200), (220) and 311 crystal faces of the fcc metallic silver, respectively. The successful impregnation of Ag NPs on the PU nanofibers was confirmed by EDS showing the presence of Ag peaks (Fig. 1b).

Fig. 2 shows the representative FESEM images at low and high magnification for the PU nanofiber membranes before and after impregnated with Ag NPs. As shown in Fig. 2a and a', the surface of neat PU nanofibers is relatively smooth and an ultra fine matrix of interlocking fibers with sub-micron sizes, high porosity, and randomly-ordered morphology was observed. From Fig 2b and b', it can be clearly seen that, after immersion in polyol medium for 20 h, the outer surfaces of PU nanofibers became significantly rough due to the uniform decoration of nanoparticles. As shown in the inset of Fig 2b', the Ag NPs with narrow size distribution were firmly attached to the fiber surfaces. Generally, in order to decorate or assemble metal NPs on surfaces of electrospun nanofibers, many of the reports used the immersion technique followed by post treatment in the presence of surfactant, sensitizing and stabilizing reagent [14-16]. However, the present PU nanofibers have been uniformly decorated by well dispersed Ag NPs without using any additional chemicals to modify the nanofiber surfaces except of ethylene glycol dispersion medium. In the present study, the possible assembly mechanism for Ag NPs on the PU nanofibers could be explained on the basis of hydrogen bonding interactions between the amide groups along the PU backbone and the hydroxyl groups capped on the surface of the Ag NPs [15]. After immersion, the PU mat turned from white to yellow and maintained this color past several washings with water (insets of Fig. 2a and 2b).

The uniformly distributed Ag NPs on the electrospun PU nanofibers can absorb analytes directly on their surfaces, leading to superior SERS sensitivity and they may provide a unique substrate for Raman applications. For this purpose 4-MBA is used as probe molecule to evaluate the SERS performance of the prepared nanostructures. As shown in Fig. 3, normal Raman scattering spectrum of 4-MBA powder as well as the SERS spectra from PU-Ag NPs nanofibrous membranes are comparable to those reported previously for 4-MBA in aqueous solution and adsorbed onto different substrates [2, 17]. In particular, characteristic vibrational modes, including ν(CC) ring-breathing (1069 cm^{-1}) and ν(CC) ring-stretching (1575 cm^{-1}) modes, which appear very weak in the Raman spectrum of 4-MBA (Fig 3a), are not only found to be remarkably enhanced in the obtained SERS spectrum of 4-MBA absorbed on the Ag/PU nanofibers (Fig 3b), but also other intense peaks, δ(CH) bends (1136 cm^{-1} and 1176 cm^{-1}) are also observed. High SERS performance of the present substrate can be explained by the electromagnetic field enhancement associated

with surface-plasmon-coupled metal NPs, which have the appropriate interparticle gap, suitable for the generation of Raman "hot spots". While the enhancement factor (EF) of SERS substrates cannot be accurately calculated due to the rough surface of the Ag/PU nanofibers, our rough estimation gave an EF value of 10^5, as compared to similar Ag/PU fibrous nanostructures reported previously [8, 11]. Besides, the distance of the probe to the metal surface has been found to play a dominant role in determining the final enhancement as reported in the earlier study [18] and successful impregnation of Ag NPs onto the surface of the PU nanofibers by simple polyol method could achieve direct contact between analyte molecules and silver. It is important that the mechanical robustness and flexibility of Ag/PU nanofiber can be tailored into any shape, which would be extremely useful for mobile SERS applications [8, 19].

Conclusion

In summary, a simultaneous synthesis and decoration of Ag NPs on the electrospun PU nanofibers fabricated by electrospinning was successfully performed via a polyol method without the need of any binding agent or surfactant except of hot ethylene glycol solution. Morphological analysis demonstrated that the Ag NPs with narrow size distribution were firmly attached to the fiber surface. Furthermore, SERS spectra showed comparatively high intensity in Raman characteristic peaks. Our present method is simple, safe and cost-effective, and the obtained composite materials may be a potential candidate as SERS substrates.

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Figure captions

Fig. 1. (a) The XRD pattern and (b) EDS spectrum of the Ag NPs impregnated electrospun PU nanofibers.

Fig. 2. The low- and high-magnification FE-SEM images of the electrospun neat and composite nanofibers: (a and a') PU; (b and b') Ag/PU.

Fig. 3. (a) Raman spectra of 4-MBA and (b) SERS spectra of 4-MBA absorbed on the Ag/PU nanofibers at concentration of 10^{-4} M.