Simple fabrication of Ag nanoparticle-impregnated electrospun nanofibres as SERS substrates

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Abstract. A facile method for the fabrication of electrospun polyurethane (PU) nanofibres impregnated with Ag nanoparticles (NPs) as an efficient and free-standing surface-enhanced Raman scattering (SERS) substrates is reported here. Electrospinning was used to produce polymeric nanofibrous matrix, while a liquid polyol(ethylene glycol) solvent 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 fibre nets. Large enhancement in Raman signals of 4-mercaptobenzoic acid analytes could be realized in the present Ag/PU nanofibres due to the presence of SERS 'hotspots' by means of appropriate interparticle gap.

Keywords. Ag nanoparticles; electrospun nanofibres; polyol; SERS.

1. Introduction

In the last decade, surface-enhanced Raman scattering (SERS) has grown to become a 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.^{1–7} 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 proceed *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 that is associated with the direct charge transfer or indirect electron–hole pair excitation processes.^{8,9}

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 'hotspots' 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 these

hotspots.^{10–13} For example, Zhang *et al*¹³ fabricated flexible and highly active/sensitive SERS substrates by electrodeless plating of Ag NPs on the surface of electrospun nanofibres *via* the seed-mediated growth process and suggested that the density and size of those deposited Ag NPs which to be controlled by experimental parameters led to the appropriate interparticle gap, suitable for the generation of Raman 'hotspots'. Furthermore, Bao *et al*¹⁴ fabricated poly(methyl methacrylate) (PMMA) nanofibres 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 economical way to mass-produce Ag/polyurethane (PU) nanofibres. The aim of the present work was to prepare efficient and free-standing SERS substrates with high enhancement factor (EF) by electrospun nanofibres 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 solvent under low temperature was 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 fibre nets.

2. Materials and methods

2.1 Electrospinning

Polyurethane (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.

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Figure 1. (a) XRD pattern and (b) EDS spectrum of the Ag NP-impregnated electrospun PU nanofibres.

Electrospinning was carried out at 11 kV, tip-to-collector distance of 15 cm and solution feed rate of 1 ml h⁻¹.¹⁵ During electrospinning, the nozzle (inner diameter = 0.51 mm) kept on moving laterally (i.e., back and forth) on its axis for a distance of 150 mm and a linear speed of 100 mm min⁻¹ controlled by LabVIEW 9.0 (National Instruments). Four millilitres of PU solution was electrospun onto a grounded flat collector, which was perpendicularly oriented to the nozzle. After electrospinning, the PU nanofibrous mat was dried at 80°C for 48 h to remove the residual solvents.

2.2 Fabrication of Ag-PU composite nanofibres

The Ag NP-impregnated electrospun PU nanofibres were performed by the polyol immersion technique, similar to our previous report.^{16,17} Briefly, electrospun PU nanofibrous mats (5 cm × 5 cm) were immersed in a previously prepared EG solution containing dissolved AgNO₃ and 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.

2.3 Characterization

The surface structure and morphology of the present sample powders 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) over Bragg angles ranging from 20° to 80°. 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) and the scattering peaks were calibrated with a reference peak from a Si wafer (520 cm⁻¹). A ×40 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 two-step route, the well-distributed assembly of Ag NPs on the electrospun nanofibres was successfully fabricated through a simple and controllable manner. The structure of the Ag/PU composite nanofibres was characterized by XRD and it is shown in figure 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 nanofibres 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 nanofibres was confirmed by EDS showing the presence of Ag peaks (figure 1b).

Figure 2 shows the representative FESEM images at low and high magnification for the PU nanofibre membranes before and after impregnated with Ag NPs. As shown in figure 2a and a', the surface of neat PU nanofibres is relatively smooth and the ultrafine matrix of interlocking fibres with submicron sizes, high porosity and randomly ordered morphology was found. After immersion in polyol medium for 20 h, the outer surfaces of PU nanofibres were significantly rough by means of impregnated with Ag nanoparticles (figure 2b). As can be clearly observed in figure 2b', the Ag NPs with narrow size distribution were uniformly decorated on the surface of nanofibres. Generally, in order to decorate or assemble metal NPs on surfaces of electrospun nanofibres, many studies reported on the use of an immersion technique followed by post-treatment in the presence of surfactant, sensitizing and stabilizing reagent.^{18–20} However, in the present study, the PU nanofibres have been uniformly decorated with well-dispersed Ag NPs without using any additional chemicals to modify the nanofibre surfaces, except for ethylene glycol dispersion medium. Here, the possible assembly mechanism of Ag NPs on the PU nanofibres could be explained on the basis of hydrogen bonding interactions between the amide groups along with the PU backbone and the hydroxyl groups capped on the surface of the Ag NPs.¹⁸ After immersion, the PU mat turned from white to yellow and maintained this colour even after several washing with water (see insets of figure 2a and b).

Figure 2. Low- and high-magnification FE-SEM images of the electrospun neat and composite nanofibres: (a and a') PU and (b and b') Ag/PU.

The uniformly distributed Ag NPs on the electrospun PU nanofibres 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-mercaptobenzoic acid (4-MBA) is used as a probe molecule to evaluate the SERS performance of the prepared nanostructures. As shown in figure 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 adsorption.^{7,21} In particular, characteristic vibrational modes, including $\nu(\text{CC})$ ring-breathing (1069 cm^{-1}) and $\nu(\text{CC})$ ring-stretching (1575 cm^{-1}) modes, which appear very weak in the Raman spectrum of 4-MBA (figure 3a), are not only found to be remarkably enhanced in the obtained SERS spectrum of 4-MBA absorbed on the Ag/PU nanofibres (figure 3b), but also other intense peaks, $\delta(\text{CH})$ bends (1136 and 1176 cm^{-1}), are observed. The 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 ‘hotspots’. While the EF of SERS substrates cannot be accurately calculated due to the rough surface of the Ag/PU nanofibres, our rough estimation gave an EF value of 10^5 , as compared to similar Ag/PU fibrous nanostructures reported previously.¹⁴ It is well accepted that the SERS enhancement is closely related to the nanostructures of the Ag NP aggregates on/in the polymeric nanofibres support.^{13,14} 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 an earlier study,^{22,23} and successful impregnation of Ag NPs onto the surface of

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

the PU nanofibres 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 nanofibre can be tailored into any shape, which would be extremely useful for mobile SERS applications.^{13,24}

4. Conclusion

In summary, simultaneous synthesis and decoration of Ag NPs on the electrospun PU nanofibres that were made by electrospinning process was successfully performed *via* the 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 fibre 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 potentially be a good candidate as SERS substrates.

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