DOI 10.5162/IMCS2018/P1OS.8

Fabrication and SERS property of Ag-coated hierarchical polyvinylpyrrolidone fibers

Xiang-Xiang Fan, Xiu-Li He, Jian-Ping Li, Xiao-Guang Gao, Jian Jia, and Zhi-Mei Qi
State Key Laboratory of Transducer Technology, Institute of Electronics, Chinese Academy of Sciences, Beijing, China, 100190
hxl@mail.ie.ac.cn

Abstract:
A new and facile strategy to fabricate Ag-coated hierarchical polyvinylpyrrolidone (PVP) fibers as a Surface-enhanced Raman scattering (SERS) substrate has been successfully developed. The fabrication process includes PVP fibers electrospinning, oxygen plasma treatment and Ag film sputtering. The effect of plasma treatment and sputtering on the morphology and the SERS activity were investigated. Because of high specific surface area and the nanoscale gaps, the SERS activity of the hierarchical fibers substrate is 16 times more than that of the raw ones. The SERS signal can still be observed with Nile Blue (NB) molecules concentration of 10^{-10} M. The SERS substrate with Ag-coated hierarchical PVP fibers has enhanced sensitivity and good uniformity and shows a promising potential for practical application.

Key words: hierarchical structure; electrospinning; plasma treatment; sputtering; surface-enhanced Raman scattering

Introduction

Surface-enhanced Raman scattering (SERS) has great potential for chemical and biological detections. Numerous researches about low cost, timesaving, controllable and large scale fabrication method of the SERS substrate have already been carried out [1]. It's still a challenge to facilely fabricate the SERS substrate with high enhancement and reproducible signal on a large scale. Recently, many reports about SERS substrate based on electrospinning have been published [2]. Preparing the hierarchical fibers with nanogaps is an effective way to increase SERS activity [3]. In this paper, a fabrication method of Ag-coated hierarchical PVP fibers was presented and a SERS substrate with tunable structure, high sensitivity and good uniformity was obtained by the facile method.

Experimental

The Ag-coated hierarchical PVP fibers were obtained as schematically shown in Fig. 1. Firstly, the PVP fibers were electrospun and dried at 80 ℃ for 1 h. The electrospinning solution was 0.4 g PVP in 5 ml ethanol and the solution feed rate was 0.3 ml/h. The applied voltage and distance between the needle and collector was 11 kV and 10 cm, respectively. Subsequently, the fibers were treated with oxygen plasma using a reactive ion etching system to obtain hierarchical PVP template. The RF voltage frequency was 13.56 MHz and the incidence power density was 0.56 W/cm^2. The chamber pressure and the flow rate of oxygen was 3 Pa and 30 ml/min, respectively. Finally, Ag film was deposited on the PVP template by RF sputtering to fabricate Ag-coated hierarchical PVP fibers. The Ag target was used and the RF power density was 1.21 W/cm^2. Argon was adopted as the working gas and the chamber pressure was 0.5 Pa.

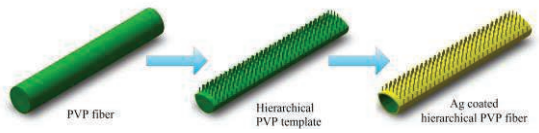

Fig. 1. Fabrication process of Ag-coated hierarchical PVP fibers.

The SERS substrate was dipped into Nile Blue (NB) solution with a certain concentration for 30 min and then dried in air before testing. The Raman scattering spectra were examined using the Raman spectrometer (AvaRaman-785TEC, Avantes) with excitation wavelength of 785 nm. The integration time was 5 s.

Results and discussion

Fig. 2 gives the structure tunability of the fabrication parameters. As shown in Fig. 2 a-c (thickness of Ag film was 60 nm), when the plasma treatment time is up to 20 s, branches

appear evidently and the gaps between the branches become obvious. With the further increase of treatment time, the gaps have a slight increase and the branches become isolated. As shown in Fig. 2 c-f (oxygen plasma treatment time was 30 s), with the rise of the Ag film thickness, the gaps between the branches decrease and the branches diameter increases. The branches keep isolated with Ag film thickness less than 60 nm. It is clear that the branches diameter and the gaps can be tuned by Ag film thickness and oxygen plasma treatment time.

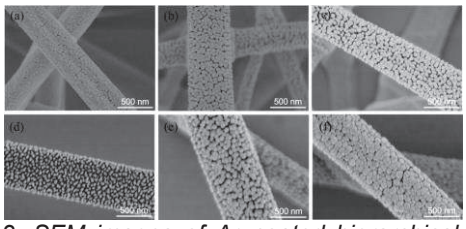

Fig. 2. SEM images of Ag-coated hierarchical PVP fibers with (a) 10 s, (b) 20 s, (c) 30 s oxygen plasma treatment, and with Ag film thickness of (d) 30 nm, (e) 90 nm and (f) 180 nm.

Fig. 3 shows the effect of the fabrication parameters on SERS activity. The peak intensity of Ag-coated hierarchical PVP fibers at 596 cm^{-1} is 16 times higher than that of the Ag-coated raw ones (Fig. 3a). The enhanced SERS activity results from the hierarchical structure. Firstly, the hierarchical structure with nanoscale branches provides high specific surface area, so more NB molecules could be absorbed on the surface of the hierarchical fibers. Secondly, the nanoscale gaps between branches can generate enhanced plasmon coupling which could highly enhance local electromagnetic field [4]. As shown in Fig. 3b and 3c, the SERS activity of the Ag-coated hierarchical PVP fibers could be modulated by the plasma treatment time and Ag film thickness. Oxygen plasma treatment time and Ag film thickness were optimized as 30 s and 60 nm, respectively.

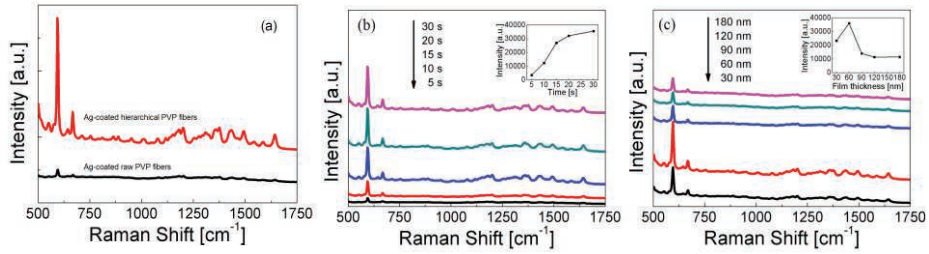

Fig. 3. SERS spectra of 10^{-6} M NB adsorbed on Ag-coated (a) hierarchical and raw PVP fibers, (b) hierarchical PVP fibers with different plasma treatment time and (c) hierarchical PVP fibers with different Ag film thickness.

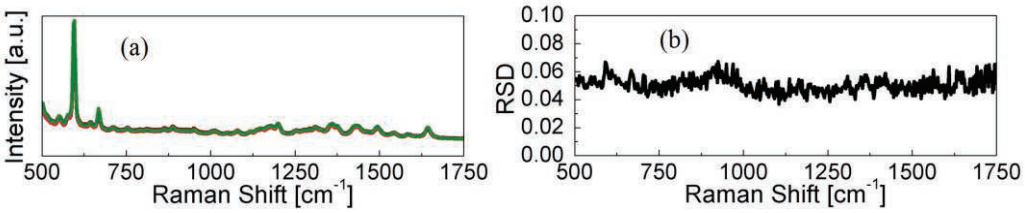

Fig. 4. (a) SERS spectra of 10^{-6} M NB at 10 different sites and (b) RSD of the spectra.

SERS spectra of NB with different concentrations were collected and the signal of NB molecules can still be observed for the concentration of 10^{-10} M. In order to investigate the uniformity of the substrate, SERS spectra of NB molecules at 10 random sites on the optimized Ag-coated hierarchical PVP fibers substrate were collected (Fig. 4). The size of the substrate is 20 mm × 20 mm. The relative standard deviation (RSD) of the spectra at 596 cm^{-1} is about 6.7%. The results reveal a good uniformity of the SERS substrate with Ag-coated hierarchical PVP fibers.

References

[1] Tian C. F., et al., Nanoparticle Attachment on Silver Corrugated-Wire Nanoantenna for Large Increases of Surface-Enhanced Raman Scattering, *ACS NANO* 5, 9442-9449 (2011); doi: 10.1021/nn203889d

[2] Zhang C. L., et al., Co-Assembly of Au Nanorods with Ag Nanowires within Polymer Nanofiber Matrix for Enhanced SERS Property by Electrospinning, *Nanoscale* 4, 5348-5355 (2012); doi: 10.1039/C2NR30736G

[3] Fathima S. J. H., et al., Surface-Structured Gold-Nanotube Mats: Fabrication, Characterization, and Application in Surface-Enhanced Raman Scattering, *Small* 6, 2443-2447 (2010); doi: 10.1002/smll.201000342

[4] Huang Z. L., et al., Improved SERS Performance from Au Nanopillar Arrays by Abridging the Pillar Tip Spacing by Ag Sputtering, *Adv. Mater.* 22, 4136-4139 (2010); doi: 10.1002/adma.201001179