Comparison of preparation methods for poly(vinyl alcohol) electrospun nanofibers embedded with Ag nanoparticles as SERS substrates

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Two main poly(vinyl alcohol)/silver (PVA/Ag) nanofibers surface-enhanced Raman spectroscopy (SERS) substrates were prepared through the combination of electrospinning and ultraviolet (UV) reduction, the properties were also compared and investigated in this work. In Method 1, PVA/AgNO$_3$ solution was reduced by UV firstly, then the PVA/Ag nanofibers were obtained by electrospinning of PVA/Ag nanoparticles (NPs) solution; In Method 2, PVA/AgNO$_3$ solution were directly to electrospin, then followed by the reduction process of UV with the PVA/AgNO$_3$ nanofibers. The PVA/Ag nanofibers were characterized by SEM, TEM, XPS, UV-vis, FTIR and wetting angle. The PVA/Ag nanofibers prepared by Method 1 retained the hydrophilic of PVA, herein, it taked less time to detect Rhodamine 6G (R6G) aqueous solution than Method 2. And the Raman spectra of probe R6G showed that the PVA/Ag nanofibers prepared by Method 1 could reach the SERS detection limit of 10^{-5} M with less AgNO$_3$ (4 wt%) than Method 2 (16 wt%). These findings provide a more effective method for the preparation of PVA/Ag nanofibers SERS substrates, and will expand the application range of PVA/Ag composite nanofibers.

1. Introduction

SERS is a promising tool for chemical analysis, and it has been widely used in analytical chemistry, environmental monitoring, and biomedicine[1]. To date, Ag nanomaterials have shown excellent SERS performance, due to its surface plasmon resonance (SPR) effect. The typical methods for Ag-based SERS substrates include chemical synthesis, physical deposition and sputtering, they also shows high SERS activity[2]. However, the low space utilization, poor flexibility of these rigid surfaces limits the applicability of these SERS substrates. Thus, electrospun nanofibers have attracted extensive attention as the supporting materials of Ag NPs due to low diameter, huge specific surface area, high porosity and three-dimensional framework. In addition, the polymer shell can protect Ag NPs from environmental effects, which ensures the long-term stability of SERS signals[3-5].

Recently, various polymers have became SERS supporting materials through electrospinning technique, for example, poly (bisphenol a carbon) (PC), poly (styrene-co-butadiene) (SB), poly (vinyl alcohol) (PVA), polystyrene (PS), polyamide (PA) and polyimide (PI). Most polymers need to use organic solvents in the dissolution process (e.g. dichloromethane, tetrachloroethane and tetrahydrofuran), which are environmentally unfriendly. PVA is a water-soluble, biocompatible polymer and exhibits high spinnability. Moreover, PVA can act not only as a supporting material, but also as a reducing agent for Ag NPs due to the hydroxyl groups[6-9].

Here, we describe two methods for embedding AgNPs into PVA nanofibers through the combination of electrospinning technique and UV reduction. The PVA nanofibers can protect Ag NPs from the influence of the environment, but the polymer must swell in the probe solution. It is important to note that, the hydrophilic of PVA/Ag nanofibers with different methods would be changed during the UV reduction. Herein, they were compared and optimized from the aspects of the amount added for $AgNO_3$, sampling and testing times, SERS performance and so on.

2. Experimental

2.1. Materials

PVA (1799, alcoholysis degree 98-99), Sodium dodecyl sulfonate (SDS, AR), $AgNO_3$ (AR), and R6G (AR) were purchased from Shanghai Aladdin reagent network, China.

2.2. Different preparation methods of PVA/Ag nanofibers

Method 1: 0.006 g SDS and 2.4 g PVA was dissolved in 30 mL water under magnetic stirring at 98 ℃ for 1 h. The $AgNO_3$ was slowly added into PVA solution after it cooled to room temperature. The mixtures were vigorously stirred for 2 h in the dark. Then, they were irradiated under the UV light for 3 h to reduce the Ag^+ to Ag NPs. The electrospun solution was injected into the syringe, and the nanofibers were collected with tin foil paper.

Method 2: The $AgNO_3$/PVA mixtures were prepared in the same manner as in Method 1. But the solution was applied to electrospin directly to prepare nanofibers. Then, the nanofibers were irradiated under the UV light for 3 h to reduce the Ag^+ to Ag NPs.
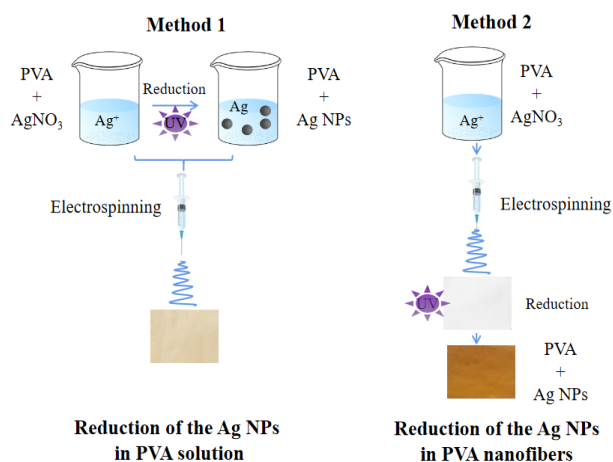

Fig. 1. Schematic illustration of methods uesed for prepare PVA/Ag nanofibers SERS substrates.

The electrospun parameters were set as follows: an applied voltage of 12 kV, a tip-to-collector distance of 15 cm, a feed rate of 1mL/h. Fig.1 shows the two methods used to prepare PVA/Ag nanofibers.

2.3. Characterization

FE-SEM (S-4800) and TEM (JEM-2800) were used to visualize the morphology of the PVA/Ag nanofibers. ATR-FTIR (vertex 70) spectra of the nanofibers were recorded between 600 cm^{-1} and 4000 cm^{-1}. UV-visible spectrometer (lambda 750s) was performed the absorbance characterization of the substrates. The SERS performance was evaluated through Raman spectrometer (DXR), with an excitation wavelength of 633 nm, laser power of 3 mW and an objective lens of $10\times$. R6G (10^{-2} M, 10^{-3} M, 10^{-4} M, 10^{-5} M) in aqueous solutions were used as probe molecule.

3. Results and discussion

The properties of the PVA solution would be change after $AgNO_3$ was added to the system or UV reduction was carried out. Indeed, we found that the electrospinning process were changed with the $AgNO_3$ contents, and the corresponding SEM and TEM images can be seen in Fig. 2.
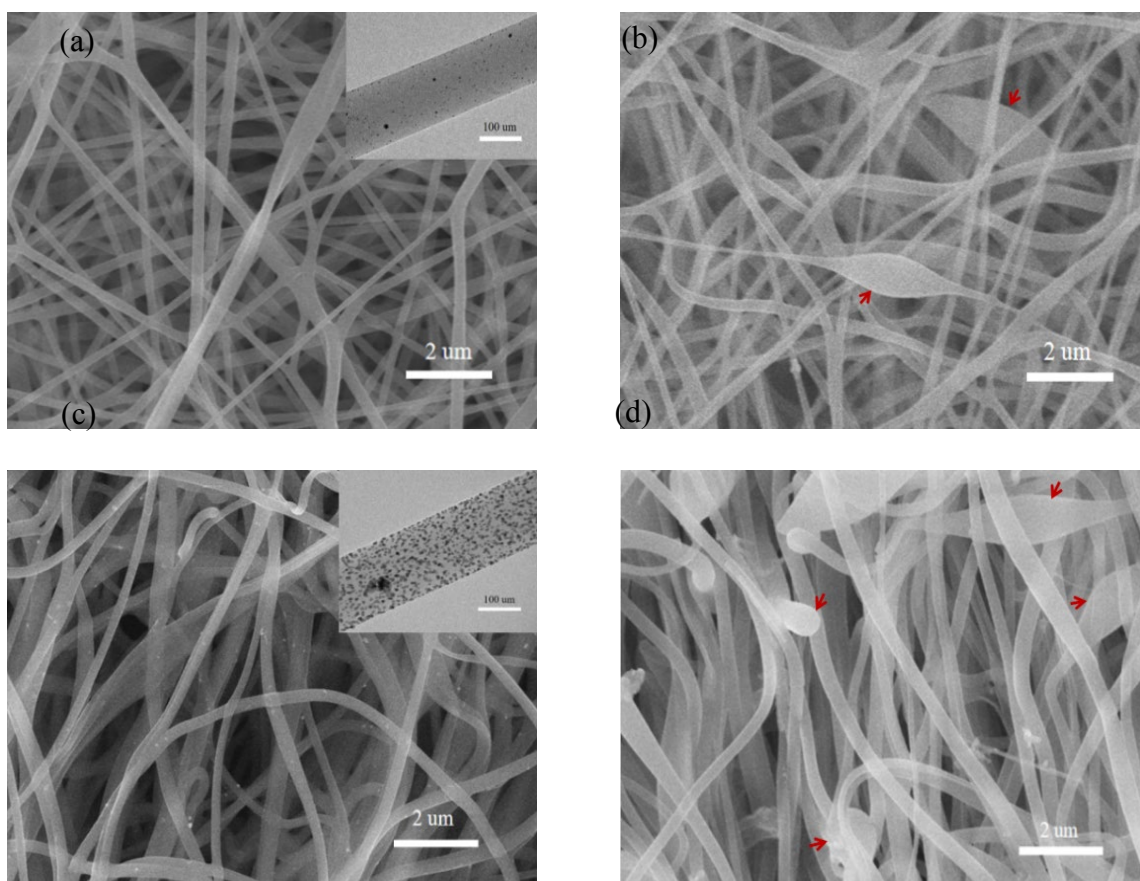

Fig. 2. SEM images of the PVA/Ag nanofibers with: (a) $AgNO_3$ content (4 wt%) and (b) $AgNO_3$

content (8 wt%) prepared by Method 1; (c) $AgNO_3$ content (16 wt%) and (d) $AgNO_3$ content (20 wt%)

prepared by Method 2; the insets were the corresponding TEM images.

The nanofibers surface prepared by Method 1 was quite smooth with AgNO$_3$ content of 4 wt% (Fig. 1a). However, numerous beads appeared on the PVA/Ag nanofibers with AgNO$_3$ content of 8 wt% (Fig. 2b). PVA/AgNO$_3$ solutions were reduced to PVA/Ag NPs solution by UV firstly, the conductivity improved with the contents of Ag NPs increasing. The fine flow falled onto the receiving plate without complete stretching due to higher conductivity, forming the beaded nanofibers. Meanwhile, Ag NPs in the solutions were easy to gather at the needle and the formation of continuous nanofibers was hindered. In contrast, in the SEM images of PVA/Ag nanofibers prepared by Method 2, the surface were smooth and exhibit porous structure with AgNO$_3$ content of 16 wt% (Fig. 1c), and beaded nanofibers would appear when it increased to 20 wt% (Fig. 1d). The content of AgNO$_3$ increased due to electrospinning process carried out with PVA/AgNO$_3$ mixed solution, which avoided the above effects of Ag NPs generated from UV irradiation on the electrospinning. Note that Ag NPs were not observed in the SEM images due to they were embedded in the nanofibers. However, Ag NPs were clearly observed in the TEM images (the insets of Fig. 1a and Fig. 1c) and it can be seen that more Ag NPs have formed by the Method 2 than the Method 1.
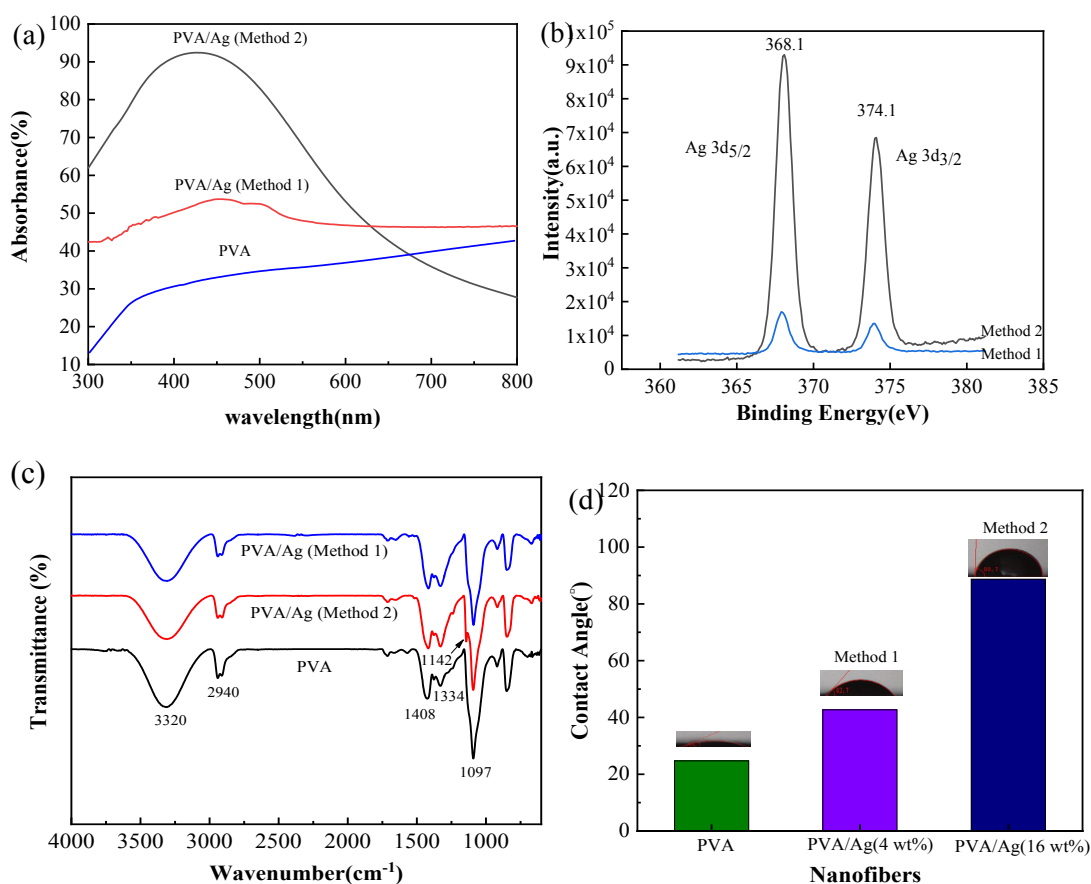

Fig. 3. (a) UV-Vis spectra of the PVA, PVA/Ag nanofibers prepared by two methods (b) XPS spectra; (c) FTIR spectra; (d) Contact angles.

Fig. 3 show the physicochemical properties of the PVA/Ag nanofibers. There were no absorption peaks in the PVA nanofibers, and the absorption peaks at 420-450 nm appeared in the PVA/Ag nanofibers prepared by the two Methods from the UV-Vis spectra (Fig.3a), which originated from the SPR effect of Ag NPs[10]. Moreover, the intensity of SPR peaks demonstrated that more Ag NPs have formed in the PVA/Ag nanofibers prepared by the Method 2 than the Method 1, which was consistent with the TEM images.

In the XPS spectra (Fig.3b), Ag3d peaks of PVA/Ag nanofibers prepared by the two Methods were presented as two peaks, one at 368.1 eV and the other at 374.1 eV, which were assigned as Ag3d5/2 and Ag3d3/2, respectively[11].

The FT-IR spectrum of PVA nanofibers (Fig.3c) showed peaks at 3320 cm^{-1}, 2942 cm^{-1}, 1408cm^{-1}, 1334cm^{-1}, and 1097 cm^{-1}, which corresponding to O-H stretching vibrations, -CH_2 stretching vibrations, O-H vibrations, C-H wagging vibrations, and C-O stretching vibrations. Note that the peak at 1142 cm^{-1} in Method 2 was associated with C-C stretching vibration, which was related to the crystallization of PVA [12,13]. Under UV irradiation for a certain time, PVA molecular chain breaked and rearranged, which can improved the crystallinity, thus change the physical properties and reduce the water solubility. In method 1, the reduction under UV light occured in the solution. Under the existence of water, the UV radiation effect of PVA decreased due to the energy of UV light attenuated. On the other hand, there were numberous hydrogen bonds between PVA molecules and H_2O molecules, which can also hinder the rearrangement and crystallization of molecular chains. Therefore, the hydrophilic of PVA was retained for the PVA/Ag nanofibers prepared by method 1, as shown in Fig.3d. The contact angles of all the nanofibers prepared were less than 90°, and the Method 1 (42.7°) was smaller than the Method 2 (88.7°). Therefore, the detection ways of probe molecules in aqueous solution were different, which would be discussed below.

A drop the R6G aqueous solution was added onto the surface of the nanofibers prepared by Method 1, during PVA swelled rapidly, Ag NPs could migrate freely and contact with R6G molecule to obtain SERS signals. Being different with the case of Method 1, in Method 2, where needed an adsorption process of soaking in R6G aqueous solution for 6 h (Fig.4a). This was because the hydrophilic of nanofibers prepared by Method 1 was much better than the Method 2.

The SERS performance of the nanofibers had been shown in Fig.4b. Clearly, there is no signals on PVA nanofibers substrate while obvious Raman signals for R6G (10^{-2} M) on PVA/Ag nanofibers substrates (Fig.4b) because of the Ag NPs embedded in PVA nanofibers forming SERS "hot spots". The Raman peaks of R6G (615cm^{-1}, 774 cm^{-1}, 1314 cm^{-1}, 1364 cm^{-1}, 1513 cm^{-1} and 1651 cm^{-1}) were in agreement with the spectra reported in the literatures[14]. The SERS signal intensity of prominent peaks (615 cm^{-1}, 1364 cm^{-1}) with the concentrations of R6G, from 10^{-2} M to 10^{-5} M, were analyzed (Fig.4c, d). As the R6G concentrations decreased, the intensities of SERS signals were weakening. The limit of detection for the two PVA/Ag nanofibers substrates were 10^{-5} M. Here, the content of $AgNO_3$ in Method 1 was only 4 wt%, while in Method 2 it reached to 16 wt%. Therefore, the best way to prepare PVA/Ag nanofibers was the Method 1, which had higher hydrophilicity and Ag NPs were easy to migrate and contact with the molecules to be tested.
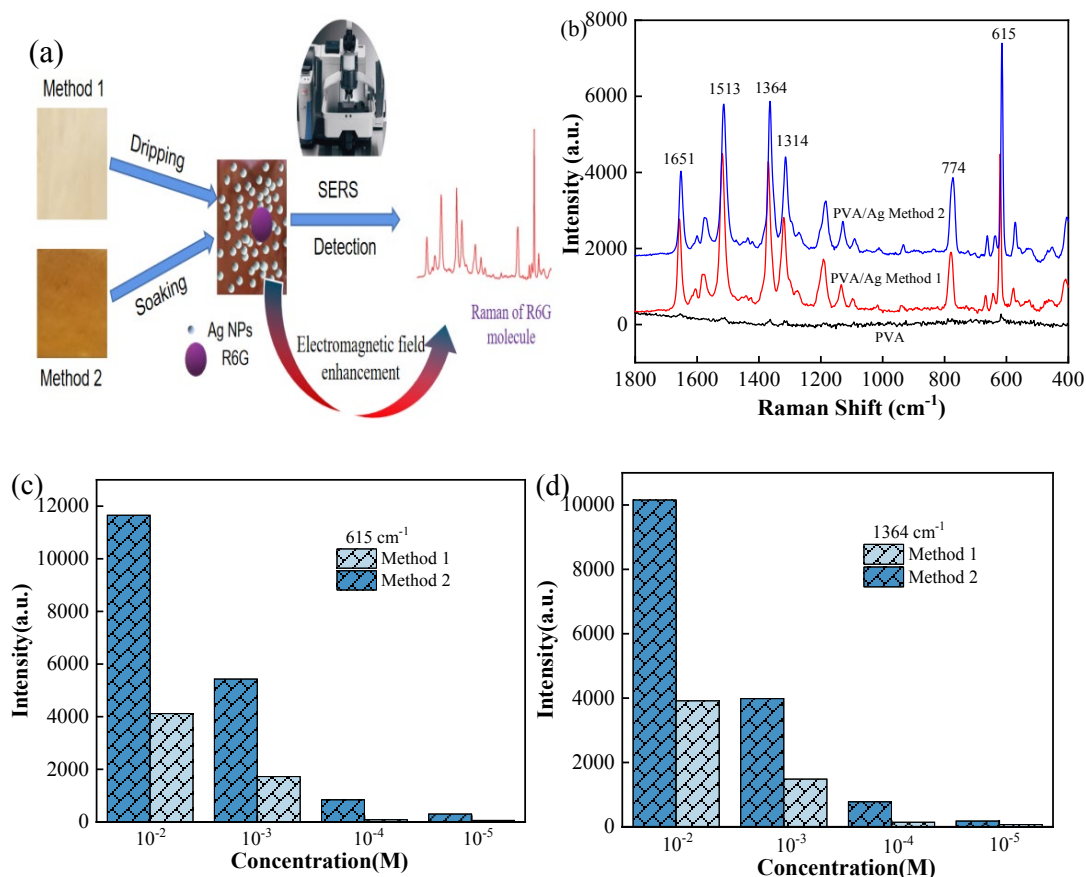
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Fig. 4. (a) SERS detection process of different substrates; (b) Raman spectra of R6G (10^{-2} M) on different substrates; The intensity of R6G with different concentrations on the two substrates at Raman shift 615 cm^{-1} (c) and 1364 cm^{-1}(d).

4. Conclusion

PVA/Ag nanofibers SERS substrates were prepared through two methods: reduction Ag NPs in PVA solution (Method 1) and reduction Ag NPs in PVA nanofibers (Method 2). The PVA/Ag nanofibers SERS substrates prepared by Method 1 not only reduced the detection time, but also achieved the same LOD (10^{-5} M) with low $AgNO_3$ content for R6G compared with Method 2. Clearly, these findings provide an effective way to prepare SERS substrates, and it has the potential for flexible materials on in-situ SERS detection.

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