Research article

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# *In-situ* electrospun aligned and maize-like AgNPs/PVA@Ag nanofibers for surface-enhanced Raman scattering on arbitrary surface

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**Abstract:** An efficient electrospun aligned surface enhanced Raman scattering (SERS) and maize-like substrate of polyvinyl alcohol (PVA) composite and Ag colloid nanofibers decorated with thermal evaporated Ag nanoparticles (AgNPs) has been developed by taking advantage of electrostatic interactions. The synergistic effects of the evaporated AgNPs (niblets) and the Ag colloid in PVA (corncob) could arouse strong electromagnetic field between the lateral and vertical nanogaps which has been demonstrated by experiment and finite-different time-domain (FDTD) simulation. In this experiment, the aligned nanofibers possesses an excellent sensitivity by detection of crystal violet (CV) and malachite green (MG) molecule at low concentration. Moreover, the proposed flexible SERS sensor was measured with outstanding uniformity and reproducibility. We also carried out *in-situ* electrospinning on a curved surface to detect the mixture of Sudan I, CV and MG molecule, which demonstrates that flexible SERS sensor, has enormous potential in accurate and *in-situ* detection on the complex geometric structure.

**Keywords:** SERS; AgNPs; PVA; aligned electrospun nanofibers; *in-situ*.

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## 1 Introduction

Surface-enhanced Raman scattering (SERS) has been regarded as one of the most powerful analytical tools for providing fingerprint information of probe molecules at the single molecular level [1–4]. To achieve ultrasensitive detection, great efforts have been made in designing and fabricating effective SERS substrate with abundant "hot spots" to dramatically enhance the local electromagnetic fields upon laser excitation [5–8]. In particular, the novel 3D porous structures used alumina [9], carbon [10] or colloidal crystals [11] as templates are newly emerged due to high specific surface area, which is useful for capturing more probe molecule and can create more "hot spots" [12, 13]. However, the approaches to fabricate these structures are high-cost and low-efficient, which greatly hinders their large-scale production in practical application. Therefore, there has been a key research interest among the researchers to develop a simple and economical way to prepare SERS substrates with a highly-controlled structure.

As a remarkable facile, novel and versatile technique for fabrication ultrafine polymeric fibrous 3D porous structures, electrospinning technique has been extensively investigated due to its template-free, flexibility and good mechanical strength [14–17]. The morphologies and diameters of electrospinning nanofibers can be controlled by varying the solution concentration, applied voltage, flow rate, tip-to-collector distance, needle type and environmental factors. As we all know, the enhanced signal amplification from SERS originates from a giant enhancement of the electromagnetic field surrounding

noble metal nanostructured materials such as gold, silver and copper [18–20]. Incorporating a metal salt into electrospun polymer nanofibers or assembling noble metal nanostructures onto the outer surfaces of the electrospun nanofibers have provided effective enhanced functionality. For instance, Wu et al. prepared $AgNO_3$/PVP and $AgNO_3$/$Ni(NO_3)_2$/PVP composites as electrospun precursors to form a porous Ag and Ag-NiO nanofiber-based SERS sensing platform for monitoring melamine and methyl parathion [21]. Kurniawan and Wang decorated the surface of electrospun PVP nanofibers with gold nanoparticles (AuNPs) by electrostatic interactions between positively charged aminosilane groups and negatively charged AuNPs, realizing the determination of methylene blue and methyl orange in spiked river water and tap water [22]. However, the size control and uniform distribution of melt nanoparticles in the polymeric nanofiber matrix are challenging, and the sensitivity of these SERS substrates remains modest owing to a limited number of the hot spots. What's more, most nanofibers decorated with metal salt or nobel metal are mostly deposited on the flat substrate.

In this study, we present a highly sensitive 3D porous maize-like SERS substrate by embedding Ag colloid into aligned electrospun PVA (a nontoxic and biocompatible polymer) nanofibers as the corncob, and decorated it with thermal evaporated AgNPs as niblets, named as "AgNPs/PVA@Ag nanofibers". Here, we have introduced two parallel copper tapes adhering to the glass as electrode to fabricate aligned nanofibers due to electrostatic interactions. Compared with traditional randomly oriented electrospun nanofibrous polymer, highly aligned electrospun nanofibers are much crucial for the homogeneous SERS signal. It is known that AgNPs exhibit excellent performance in optical absorption and scattering signatures [23, 24]. Interestingly, the electromagnetic field can be both enhanced in the lateral nanogaps between the evaporated AgNPs (niblets) on the surface and the vertical nanogaps between the evaporated AgNPs (niblets) and the Ag colloid in the corncob [25], which can significantly increase the sensitivity of the proposed maize-like SERS substrate. To demonstrate the SERS activity, the proposed electrospun composite material has been successfully applied to sensitively detect crystal violet (CV) and malachite green (MG) at low concentration owing to the dense hot spots excited by the synergistic effects of the lateral and vertical electromagnetic field enhancement, which is also proved by FDTD simulations. Furthermore, we fabricated the electrospun nanofibers of AgNPs/ PVA@Ag nanofibers on the curved surface with an *in-situ* method and successfully achieved the detection for the mixture of Sudan I, CV and MG molecule, which demonstrates its great potential for the volume production of the SERS substrate with an inexpensive and *in-situ* method on arbitrary surface and can promote the development of the accurate and *in-situ* detection on the complex geometric structure.

# 2 Materials and methods

## 2.1 Materials

Acetone ($CH_3COCH_3$, 99.5%), ethylene glycol ($C_2H_6O_2$, 99.0%), alcohol ($C_2H_6O$, 99.7%) and silver nitrate ($AgNO_3$) were purchased from local chemical plant. Polyvinylpyrrolidone (PVP, Mw = 55,000) was purchased from Sigma-Alorich. Polyvinyl alcohol (PVA, 87–89% hydrolyzed, MW 44.05) was purchased from Aladdin Co., Ltd. Ag wire (99.99%, 0.2 mm diameter) was purchased from Sinopharm chemical reagent Co., Ltd. CV (AR, 100 g) was purchased from Yuanye biotechnology Co., Ltd (Shanghai). MG (AR, 25 g) was purchased from Aladdin industrial corporation (Shanghai). The quartz glass substrate and copper tape were both obtained from commercial sources.

## 2.2 Preparation of the highly sensitive 3D porous AgNPs/PVA@Ag nanofibers SERS substrates

The preparation of the hybrid structure is shown in Figure 1. The silver colloid nanoparticles (20 wt%) were fabricated by a chemical reduction method as described in our previous work [26], and the concentration of Ag colloid during the experiment is the same. First, PVA aqueous solution with concentration of 15 wt% was prepared by fully dissolving PVA powder in deionized (DI) water at 80°C under constant stirring for 6 h. Subsequently, silver colloid with different concentration was added into PVA solution, and uniformly mixed with magnetic stirrer for 1 h. After that, the sample solution was poured into a 10 ml syringe fitted with 19 G blunt end stainless steel needle connected to the positive electrode. A clear glass sheet was covered by two parallel copper tapes separated by 1 cm as a collector, which was attached to a negative electrode. The oriented nanofibers were contributed from electrostatic interactions. The tip-to-collector distance was fixed at 10 cm, applied voltage was 12 kV, a flow rate was 2 mm/h with temperature at 35°C and humidity of 30% for the electrospinning process, and the electrospinning time was controlled at 20 min. Then the sample of

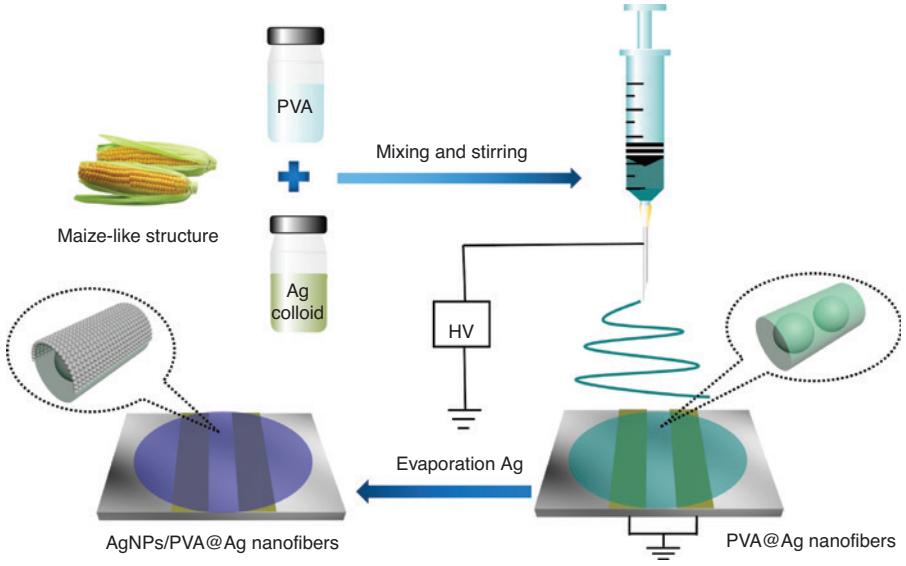


**Figure 1:** Schematic illustration of the process for the synthesis of the highly sensitive 3D porous AgNPs/PVA@Ag nanofibers SERS substrates.

Ag colloid embedded in PVA (PVA@Ag nanofibers) was obtained. Finally, the small-size AgNPs was deposited on the PVA@Ag nanofibers substrate using thermal evaporation process with Ag wires (length of 1 mm, diameter of 0.2 mm) to obtain AgNPs/PVA@Ag nanofibers SERS substrates.

### 2.3 Apparatus and characterization

The morphologies of the prepared samples were characterized by the scanning electron microscope (SEM ZEISS Sigma500) with energy dispersive spectrometer (EDS). All the SEM images in the paper are measured at 10 kV voltage.

To study the SERS behaviors of the proposed AgNPs/PVA@Ag nanofibers SERS substrate, we chose the Raman spectrometer (Horiba HR Evolution 800) with the excited laser of 532 nm and the excitation of 0.48 mW to collect the SERS spectra. The diffraction grid was 600 g/nm, and the integration time was 8 s. The laser light was coupled through an objective lens of 50×.

### 2.4 Theoretical simulation

In theoretical simulations, a commercial FDTD software package, FDTD Solutions based on 3D Maxwell's solver and provided by Lumerical Solutions Inc. was used to calculate the local electric field distributions. The illumination source was the incident plane wave composed by superposition of transverse polarization component (TM) and transverse electric field component (TE). The absorption boundary condition is the perfect matching layer (PML). Here, the laser of 532 nm wavelength was chosen as excitation light and the refractive index of PVA is set as 1.4835.

## 3 Results and discussion

The aligned electrospun nanofibers of Ag colloid embedded into 15 wt% PVA aqueous solution with different PVA/Ag volume ratio of 2:1, 1:1, 1:2; 1:3 were characterized by SEM, as shown in Figure 2A–D. It can be seen clearly that there are some spheres (Ag) in nanofibers resulted from the addition of Ag colloid solution. The amount of Ag remarkably increases as the concentration of Ag colloid solution in the electrospun PVA nanofibers increase. The sparse Ag with poor homogeneity in the PVA nanofibers at volume ratio of 2 (PVA):1 (Ag colloid) was observed in Figure 2A, due to the small amount of Ag colloid solution. In Figure 2B, the Ag has become more intensive than that in Figure 2A, while the nanofibers have uneven thickness owing to the change of the concentration of the whole solution. The relative uniform Ag and PVA aligned nanofibers in Figure 2C can be profited from the perfect volume ratio of PVA and Ag colloid, which is conducive to the generation of uniform electromagnetic field and will be discussed in the following section. The inset of Figure 2C is the detailed SEM of PVA@Ag nanofibers. In this case, the diameters of electrospun nanofibers are about 100 nm on the average. While in Figure 2D, the nanofibers appeared adhesion, and abundant Ag aggregated together, which

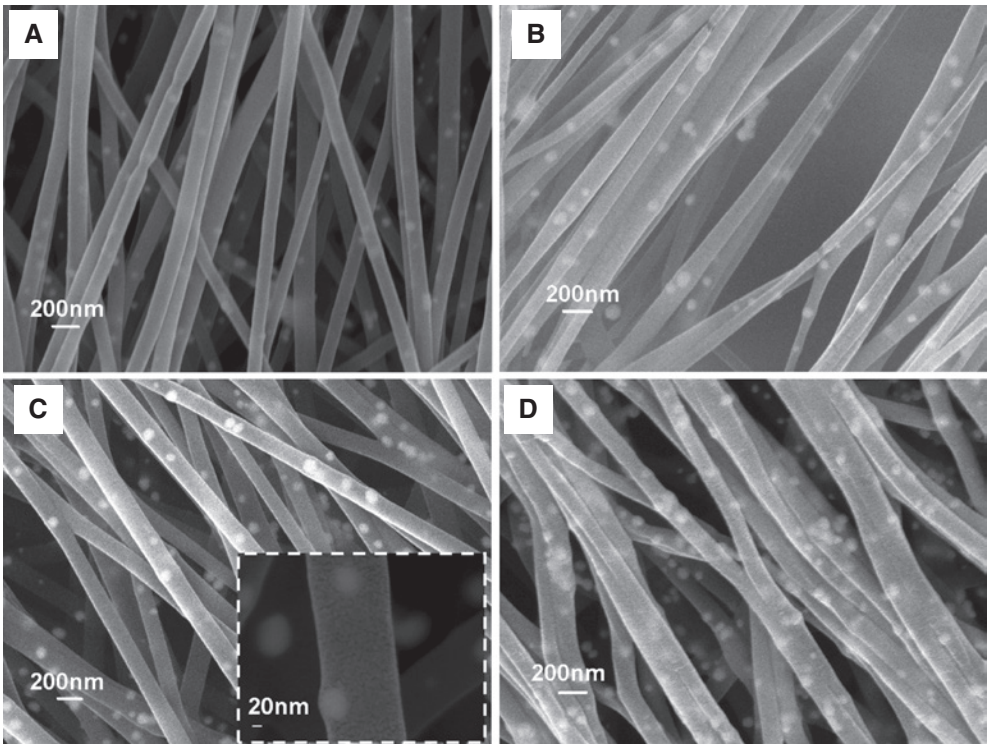


**Figure 2:** Morphology of aligned PVA@Ag nanofibers.
SEM morphology characterization from PVA@Ag nanofibers with volume ratio of (A) 2 (PVA):1 (Ag colloid), (B) 1 (PVA):1 (Ag colloid), (C) 1 (PVA):2 (Ag colloid), (D) 1 (PVA):3 (Ag colloid), respectively. The inset of Figure 2C is the detailed SEM of PVA@Ag nanofibers.

can be attributed to the excess amount of Ag colloid solution.

The assembled substrate of PVA nanofibers mixed with Ag colloid could be used SERS detection for molecular sensing with local electromagnetic field. The SERS measurements used CV alcoholic solution as probing molecules were carried out to optimize the PVA/Ag volume ratio and study the enhancement effects of the aligned electrospun PVA@Ag nanofibers. Figure 3A exhibits the SERS spectra of $10^{-5}$ M CV molecules absorbed on PVA@Ag nanofibers with different PVA/Ag volume ratio corresponding to that in Figure 2A–D. It reveals that the best SERS performance for CV detection is collected on the substrate with PVA/Ag volume ratio of 1:2. In order to demonstrate the optimal SERS enhancement effect directly and conveniently, the relative intensity of the characteristic peaks with error bar (same batch but different positions) at 917, 1179, and 1593 $cm^{-1}$ corresponding to different PVA/Ag volume ratio was collected to plot the histogram as presented in Figure 3B. Obviously, the maximum intensities

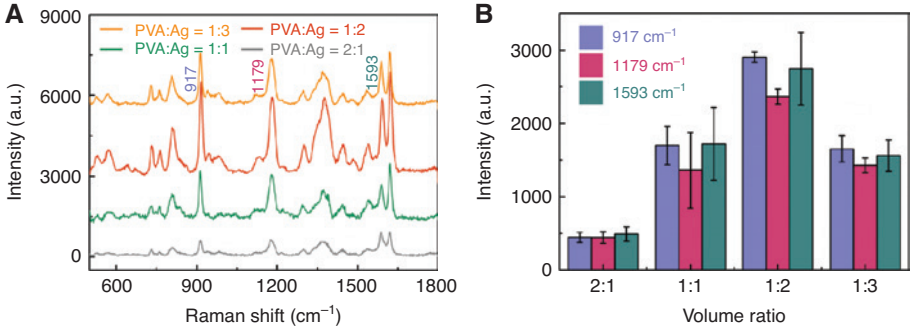


**Figure 3:** Influence of the PVA/Ag volume ratio for the SERS activity.
(A) Raman spectra of CV molecules ($10^{-5}$ M) detected on PVA@Ag nanofibers substrate with different PVA/Ag volume ratio. (B) The intensity of the CV at 917 $cm^{-1}$, 1179 $cm^{-1}$, and 1593 $cm^{-1}$ peak changes as a function of volume ratio on PVA@Ag nanofibers substrate.

for all of the characteristic peaks were based on the PVA/Ag volume ratio of 1:2, which suggests the optimum SERS effect can be attributed to the aligned nanofibers and the denser Ag generating more "hot spots". The difference of the enhancement for the 917, 1179, and 1593 $cm^{-1}$ may be due to the different assignment of the peaks, which is acceptable and has almost no influence for the molecular identification. Therefore, we maintained the optimum PVA/Ag volume ratio of 1:2 to further research throughout the following experiments.

To further improve the SERS activity, we deposited the AgNPs on the PVA@Ag nanofibers using a thermal evaporation process and constructed a maize-like structure, where the PVA@Ag nanofibers can be regard as the corncob and the thermally deposited AgNPs can be treated as niblets. The advantage of this maize-like structure for the SERS activity will be discussed in the following section. The representative morphologies of the aligned electrospun AgNPs/PVA@Ag nanofibers with different enlargement factor were shown in Figure 4B–D. The SEM image at low magnification in Figure 4B presents the high degree of nanofiber alignment by employing two copper tapes as conducting plates since electrostatic interactions [27], and only speckled Ag embedded into PVA nanofiber can be seen due to the too low magnification. With a larger enlargement factor as shown in Figure 4C, the dense little AgNPs on the surface of PVA nanofiber are clearly visible, and the average size of large Ag in PVA was counted by the image processing software Nano Measurer of 72 nm (the inset of Figure 4C). Further, from the Figure 4C, we can observe clearly in Figure 4D that the uniaxially aligned PVA nanofibers are uniformly covered with densely packed AgNPs with average diameter of 7 nm (the inset of Figure 4D), which is similar to the structure of the niblets on the corncob. The local composition of the AgNPs/PVA@Ag nanofibers sample is also measured with EDS elements

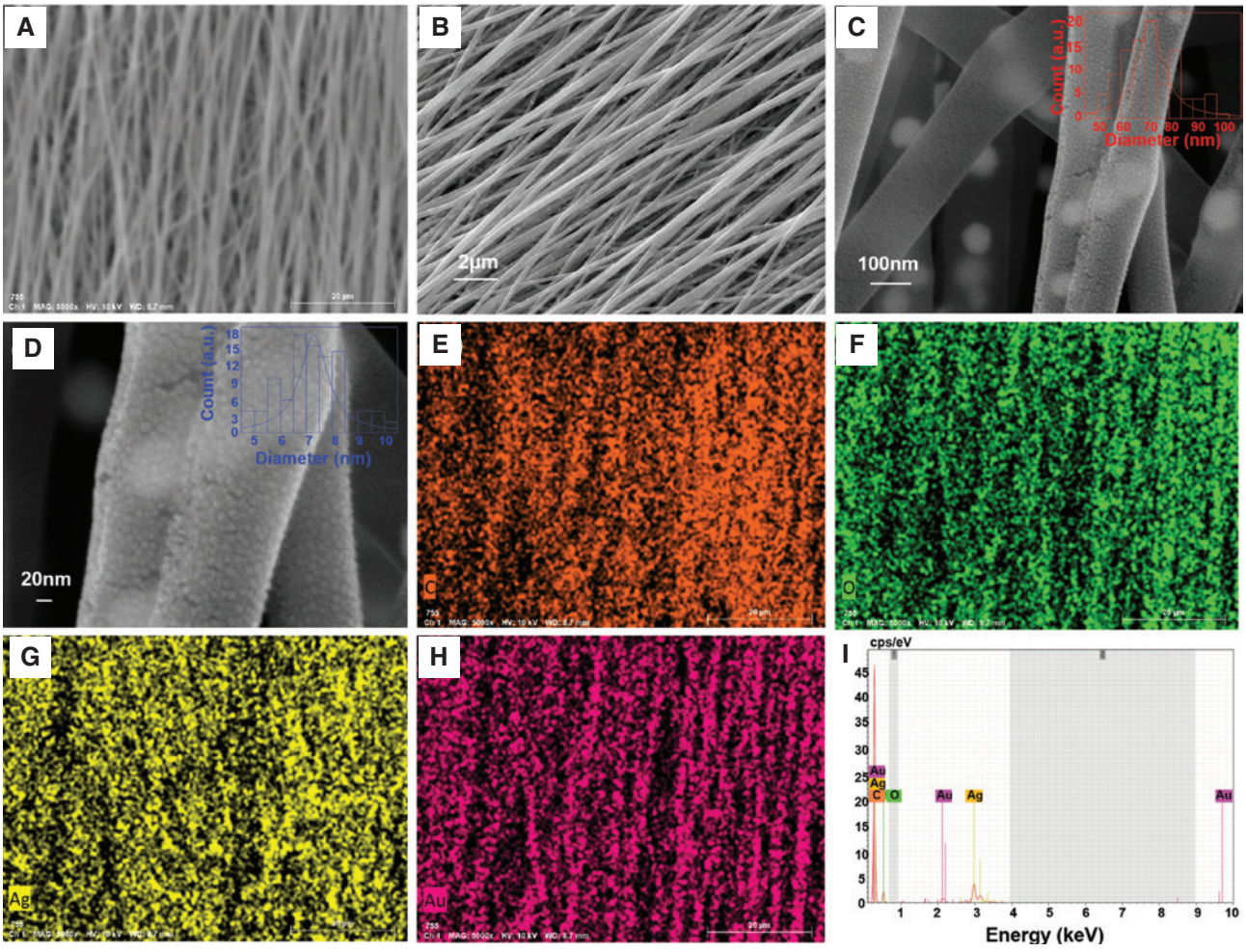


**Figure 4:** Structural characterization for AgNPs/PVA@Ag nanofibers.
(B–D) SEM images of AgNPs/PVA@Ag nanofibers electrospun hybrid films with different enlargement factor. EDS elemental maps from (E) C, (F) O, (G) Ag, (H) Au on the (A) AgNPs/PVA@Ag nanofibers substrate. (I) The EDS of the AgNPs/PVA@Ag nanofibers.

mappings shown in Figure 4E–H, which clearly revealed the presence of C (orange), O (green), Ag (yellow) and Au (red) in the substrate. The elements of C and O derive from the PVA, Au stems from sputtering on the substrate before SEM measure, and Ag element comes from the Ag embedded in the PVA nanofiber and AgNPs evapordined on the surface of the PVA. Furthermore, Figure 4I showed the energy dispersive spectrum of the AgNPs/PVA@Ag nanofibers sample, and the sharp peaks of Au, Ag, C and O further confirm the composite structure of AgNPs and PVA.

In addition, the element content of C, O, Au and Ag from PVA@Ag nanofibers and AgNPs/PVA@Ag nanofibers substrate are measured, respectively in Supplementary Tables 1 and 2. In PVA@Ag nanofibers substrate, Au element accounts for 1.27% of the overall content, and Ag element constitutes 5.63%. The Ag/Au element content ratio is about 4.43. While in AgNPs/PVA@Ag nanofibers substrate, the Ag element content is as high as 6.55% to Au element of 0.56% which is about 11.70 times, much higher than that in the PVA@Ag nanofibers substrate, because plenty of AgNPs exist on the surface of PVA nanofibers.

To test the SERS performance of PVA@Ag nanofibers substrate, the corresponding SERS spectra of CV molecule with different concentration were collected on the substrate as shown in Figure 5A. The spectra demonstrated the sensitivity of this substrate by detecting CV at a concentration as low as $10^{-8}$ M, and the dominant peaks at 917 $cm^{-1}$, 1179 $cm^{-1}$, 1376 $cm^{-1}$, 1593 $cm^{-1}$ and 1625 $cm^{-1}$ can still be distinguished at this concentration, which can be attributed to the electromagnetic field enhancement from the Ag providing rich SERS hot spots in the PVA@Ag nanofibers (corncob) and confirms a relatively high sensitivity, and the laser can penetrate the exterior PVA nanofiber easily to access the imbedded Ag to arouse the plasmonic resonance. Furthermore, to investigate the best SERS effect of composition of AgNPs and PVA and demonstrate the advantage of this maize-like structure for the SERS activity, CV molecule at concentration of $10^{-5}$ M, respectively was detected on AgNPs/PVA@Ag nanofibers, AgNPs/PVA, PVA@Ag nanofibers and planar PVA@Ag in Figure 5B. Compared with the planner PVA@Ag, the electrospunning PVA@Ag nanofibers substrate has

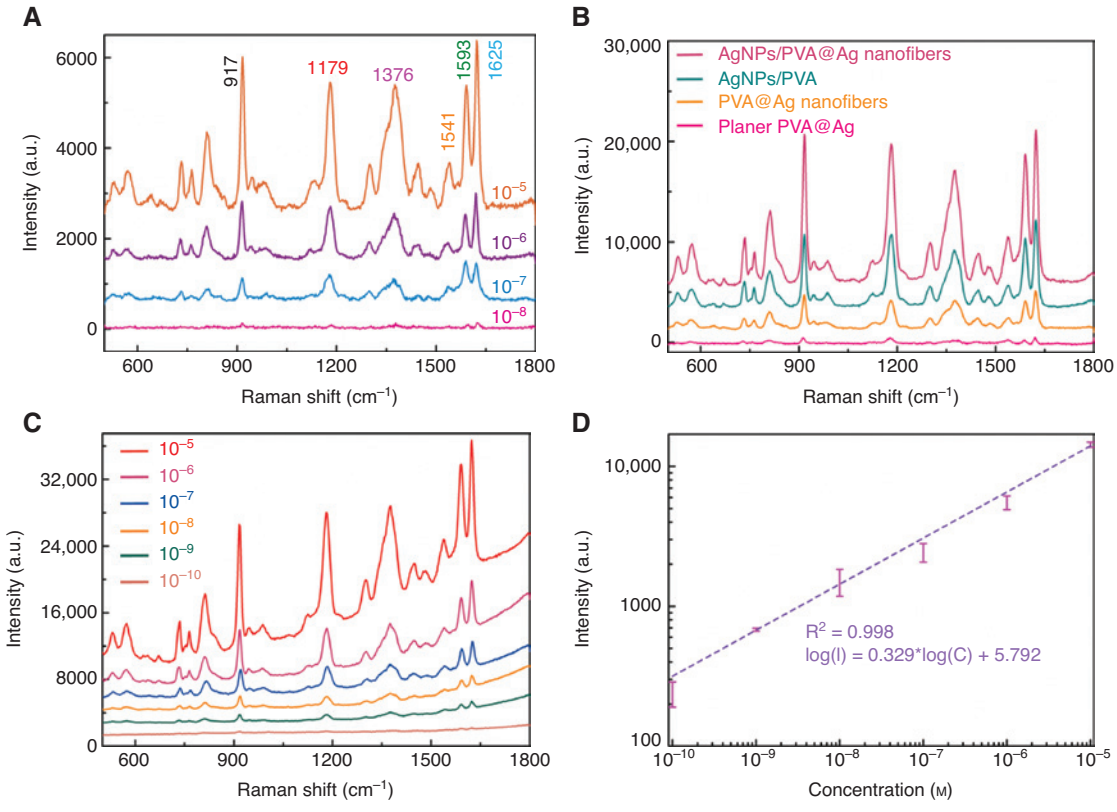


**Figure 5:** SERS performance on different substrates.
(A) SERS spectra of CV with concentrations from $10^{-5}$ to $10^{-8}$ M on the PVA@Ag nanofibers substrate. (B) Raman spectra of CV molecules ($10^{-5}$ M) detected on AgNPs/PVA@Ag nanofibers, AgNPs/PVA, electrospunning PVA@Ag nanofibers and planar PVA@Ag sample. (C) SERS spectra of CV with concentrations from $10^{-5}$ to $10^{-10}$ M on the AgNPs/PVA@Ag nanofibers substrate. (D) Linear relationships ($R^2 = 0.998$): Raman intensities at 914 $cm^{-1}$ as a function of the concentrations of CV molecules on the AgNPs/PVA@Ag nanofibers sample.

higher SERS signal, benefiting from 3D porous structures, which can capture more molecule and create more "hot spots" from the maize-like structure. Besides, the sample of thermal evaporated AgNPs on the surface of PVA has better SERS performance than that of Ag embedded in the PVA nanofiber, which is attributed to more intensive AgNPs on the surface and narrower spacing between them. Overall, the SERS intensity of prepared AgNPs/PVA@Ag nanofibers sample is the highest, that benefits not only from the electromagnetic field enhancement from the lateral nanogaps between the evaporated AgNPs (niblets) on the surface and between the Ag colloid in the corncob, but also more importantly by the vertical electromagnetic field enhancement between the evaporated AgNPs (niblets) and the Ag colloid in the corncob. In order to further investigate the excellent SERS performance of the AgNPs/PVA@Ag nanofibers structure, the Raman spectra of CV molecules with different concentrations (from $10^{-5}$ to $10^{-10}$ M) on the hybrid substrate are shown in Figure 5C. The major characteristic peaks at 917 $cm^{-1}$ and 1179 $cm^{-1}$ (ring skeletal vibration of radical orientation), 1376 $cm^{-1}$ (Ph-$C^{+}$-Ph bend, N-phenyl stretching), 1593 $cm^{-1}$ and 1625 $cm^{-1}$ (the ring C-C stretching) are clearly distinguished at concentration from $10^{-5}$ M to $10^{-9}$ M [28, 29]. The SERS intensity of the spectrum with $10^{-10}$ M is very weak, and only the spectrum at 917 $cm^{-1}$, 1583 $cm^{-1}$ and 1625 $cm^{-1}$ have slight bulge, which has reached the lowest detection limit of CV molecule. Figure 5D presents the intensity with error bar (same batch but different positions) of CV at 917 $cm^{-1}$ for different concentrations under the log scale, which fits the linearity well with correlation coefficient ($R^2$) of 0.998, and the slope presenting the sensitivity is 0.329. These results mentioned above adequately prove that hybrid aligned electrospun nanofibers have the capability to act as a good SERS-active substrate, and can realize quantitative detection utilizing the AgNPs/PVA@Ag nanofibers sample.

To assess the SERS performances of the electrospun AgNPs/PVA@Ag nanofibers substrate, the enhancement factor (EF) was evaluated using the formula [30]:

$$\mathrm{EF} = \frac{I_{\mathrm{SERS}} / N_{\mathrm{SERS}}}{I_{\mathrm{RS}} / N_{\mathrm{RS}}}. \quad (1)$$

where $I_{\mathrm{SERS}}$ and $I_{\mathrm{NR}}$ are SERS and normal Raman intensities of CV molecules, respectively acquired under identical conditions. $N_{\mathrm{SERS}}$ and $N_{\mathrm{RS}}$ refer to the average number of molecules within the laser spot for SERS and Raman intensities experiments. In order to simplify, the value of $N_{\mathrm{RS}}/N_{\mathrm{SERS}}$ was estimated from the ratio of the respective molecule concentrations [31]. $I_{\mathrm{SERS}}$ (~145) was the intensity of CV molecule at $10^{-10}$ M absorbed on the AgNPs/PVA@Ag nanofibers substrate, and $I_{\mathrm{NR}}$ (~24) was obtained for $10^{-2}$ M CV molecule adsorbed onto the silicon wafer. Consequently, the EF of this AgNPs/PVA@Ag nanofibers sample can be calculated as $6.04 \times 10^{8}$. Compared with other electrospun substrates in Table 1, AgNPs/PVA@Ag nanofibers possess higher EF and sensitivity by virtue of the maize-like structure.

Except for the sensitivity, the homogeneity and reproducibility of the aligned electrospun AgNPs/PVA@Ag nanofibers substrate plays an important part in practical applications as well, which is investigated in this paper. Figure 6A shows the Raman spectra of CV ($10^{-6}$ M) randomly collected 15 spots on the AgNPs/PVA@Ag nanofibers substrate, where the intensity of SERS signal is similar from different locations. In order to directly compare the fluctuate of the peak, the intensity distributions of the 917, 1179, 1593, and 1625 $cm^{-1}$ peaks of CV molecule from these Raman spectra was shown in Figure 6B. It reveals that the intensity of these peaks are almost on a horizontal line, and the relative standard deviation (RSD) of the Raman peaks at 917, 1179, 1593, and 1625 $cm^{-1}$ are respectively 6.926%, 15.603%, 17.998%, and 18.846%, which is much lower than the scientific standards (20%) reported by Natan on account of the aligned nanostructure [33]. Figure 6C presents the intensity distribution with error bar (from 10 spots on one sample) of the 917 $cm^{-1}$ peaks respectively collected from 10 different batches AgNPs/PVA@Ag nanofibers substrate. The mazarine line represents the average intensity of 5571.70 a.u. from the 10 batches substrate, and the fluctuation is around the mean value up and down with RSD of 12.89%, revealing the as-prepared aligned AgNPs/PVA@Ag nanofibers with outstanding reproducibility.

To investigate the potential of the AgNPs/PVA@Ag nanofibers platform in practical application, the SERS

**Table 1:** The sensitivity of different flexible SERS substrates.

| Substrate | Analytes | EF | References |
|---|---|---|---|
| Porous Ag/PVP | Rhodamine 6G | $1.59 \times 10^{5}$ | [21] |
| Si nanowire paper (SiNWP) modified with Au nanoparticle | Rhodamine 6G | ~$10^{5}$ | [31] |
| Au-coated electrosprayed organic semiconductor films (Au@BDY-4T-BDY) | Methylene blue | $1.7 \times 10^{6}$ | [32] |

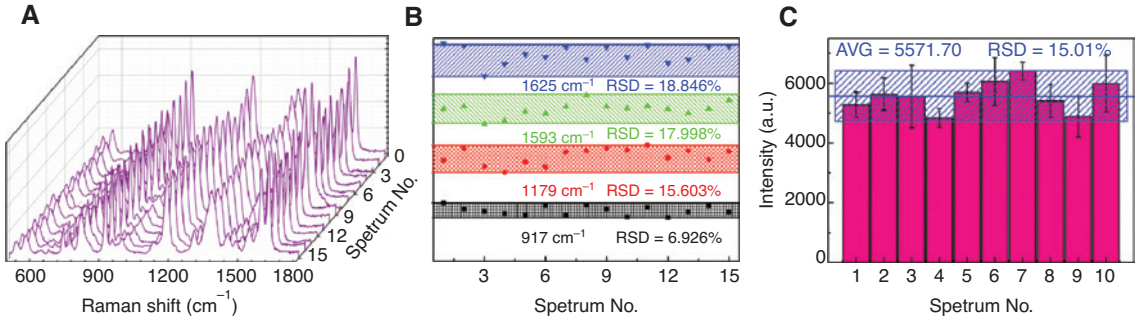


**Figure 6:** Homogeneity and reproducibility detection on the AgNPs/PVA@Ag nanofibers.
(A) The Raman spectra of CV ($10^{-6}$ M) randomly collected on the AgNPs/PVA@Ag nanofibers substrate. (B) The intensity distributions of the 917, 1179, 1593, and 1625 $cm^{-1}$ peaks for CV from (A). (C) The intensity distribution of the 917 $cm^{-1}$ peaks of CV ($10^{-6}$ M) respectively collected from 10 different batches AgNPs/PVA@Ag nanofibers substrate.

detection for MG molecule, a chemical of poisonous triphenylmethane [34, 35], was carried out. As shown in Figure 7A, the typical Raman peaks of MG at 1179, 1372, and 1625 $cm^{-1}$ have a sharp form at high concentration of $10^{-5}$ M. The band intensity weakens with the decrease of the MG concentrations and the main characteristic peaks such as 1372, 1595, and 1625 $cm^{-1}$ could be observed at concentration lower down to $10^{-9}$ M. Moreover, the linear fit calibration curve ($R^2 = 0.977$) with error bars (same batch but different positions) is illustrated in Figure 7B. The intensities of the SERS spectra of MG are proportional to the logarithm of the concentrations of the MG. Therefore, the proposed substrate shows great potential for identifying trace molecules duo to dense "hot spots"

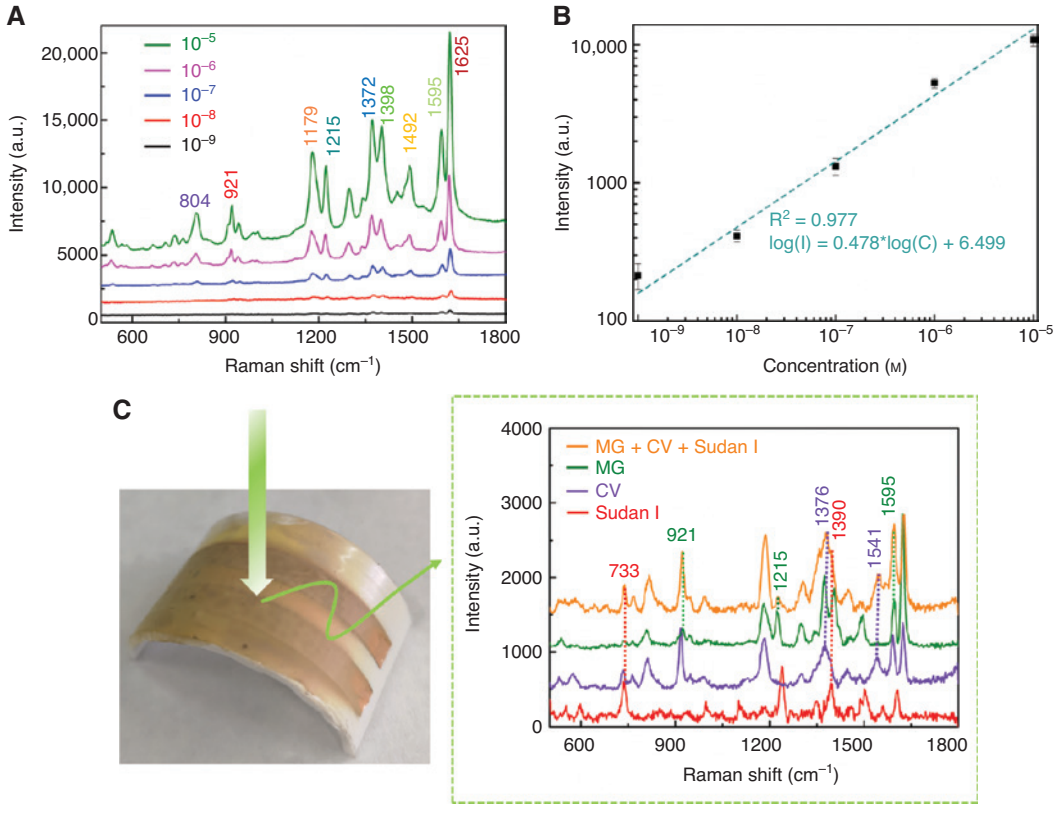


**Figure 7:** Practical application of the designed SERS substrate onto arbitrary surface.
(A) The Raman spectra of MG (concentration from $10^{-5}$ to $10^{-9}$ M) on the AgNPs/PVA@Ag nanofibers substrate. (B) Raman intensity of MG (at 1618 $cm^{-1}$) on the substrate as a function of the molecule concentration. (C) SERS spectra of Sudan red I ($10^{-6}$ M, red line), CV ($10^{-9}$ M, purple line), MG ($10^{-7}$ M, green line) and their mixtures (orange line) detected on the *in-situ* electrospinning AgNPs/PVA@Ag nanofibers substrate.

and the multiple nanogaps between particles with different sizes. Furthermore, the *in-situ* aligned electrospinning of the AgNPs/PVA@Ag nanofibers on curved surface was carried out. The photo of the substrate evaporated AgNPs was shown in the left of Figure 7C. The $10^{-6}$ M Sudan I carcinogenic molecule, $10^{-9}$ M CV and $10^{-7}$ M MG molecule was detected on the flexible substrate illustrated in the right of Figure 7C, and the peaks of CV and MG have similar intensity with that on glass as shown above, because there is no influence in the laser area. We further used the proposed flexible AgNPs/PVA@Ag nanofibers substrate to detect the more complicated sample matrices composed by the Sudan I ($10^{-6}$ M), CV ($10^{-9}$ M) and MG molecule ($10^{-7}$ M). The red dashed line present the corresponding characteristic peak of Sudan I, and its peaks at 733 $cm^{-1}$ and 1390 $cm^{-1}$ arose from ring breathing and C=C bonds in the benzene rings [36]. The purple dashed line was the peaks of CV molecule at 1376 $cm^{-1}$ and 1541 $cm^{-1}$, and green dashed line showed the presence of MG at 921 $cm^{-1}$, 1215 $cm^{-1}$ and 1595 $cm^{-1}$. It is worth noting that there are some same peaks at 1179 $cm^{-1}$ and 1625 $cm^{-1}$ for CV and MG. In a word, the result suggests this excellent flexible AgNPs/PVA@Ag nanofibers SERS substrate has a potential possibility for the application for *in-situ* detection of some toxic biochemical molecules.

To better understand the enhancement mechanism of this AgNPs/PVA@Ag nanofibers SERS-active substrate, the local electric field distributions in these structures was analyzed by the FDTD simulations. The diameter of inlaid Ag, superficial AgNPs and PVA nanofiber was 72 nm, 7 nm, and 100 nm, respectively and the space between adjacent superficial nanoparticles and between inlaid nanoparticles was set as 3 nm and 10 nm, which is in keeping with the actual size in SEM. The incident light is 532 nm and the refractive index of PVA is 1.4835 [37] according to the actual experiments. Figure 8A shows the local electric field distributions at y-z cross-section, and the electric field distributed around the AgNPs owing to the LSPR effect of AgNPs. Just as we all know, the dense hot spots distribute in the lateral nanogaps between the evaporated AgNPs (niblets) on the surface. In particular, the vertical electric field between the evaporated AgNPs (niblets) and the Ag colloid in the corncob has strong enhancement, obviously shown in Figure 8B at y-z cross-section. Therefore, the theoretical results demonstrate the strong electric fields enhancement can be excited by combining the evaporated AgNPs (niblets) with the Ag colloid in the corncob and constructing the maize-like structure on the proposed substrate and is well consistent with the experiment in Figure 5B, where AgNPs/PVA@Ag nanofibers possess the highest sensitivity compared with AgNPs/PVA, electrospunning PVA@Ag nanofibers and planar PVA@Ag sample only with monophyletic nanoparticles, which will contribute to the excellent SERS behavior of this SERS-active substrate.

## 4 Conclusion

In this study, we have prepared aligned maize-like AgNPs/PVA@Ag nanofibers using electrospinning technology by means of the integration of the PVA solution and the Ag colloid decorated with thermal evaporating silver nanoparticles. Owing to the dense hot spots excited by the lateral and vertical nanogaps proved by FDTD simulations, this composite nanofibrous substrate for detection Raman probing molecules (CV and MG molecule) exhibited excellent enhancement effect, outstanding

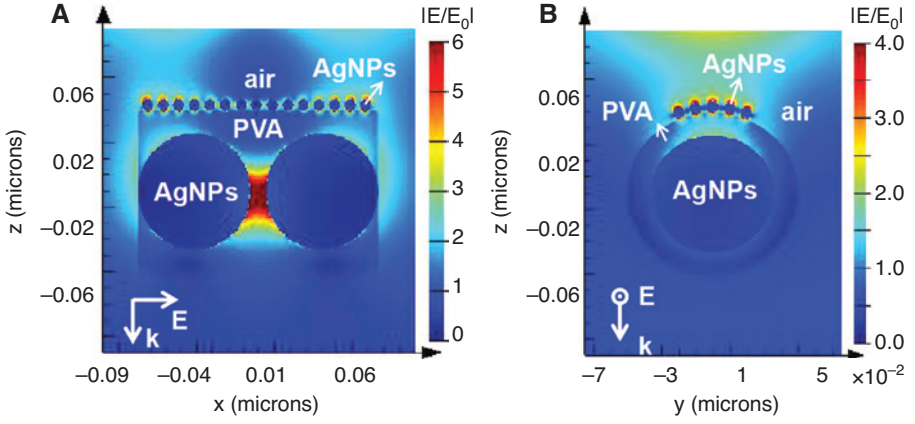


**Figure 8:** FDTD simulation results of the local electric field distribution.
(A) The local electric field distributions for the AgNPs/PVA@Ag nanofibers substrate from (A) x-z cross-section and (B) y-z cross-section. The direction of polarization and incident light is x and negative z direction in all theoretical calculations, respectively.

uniformity and reproducibility. Additionally, the *in-situ* electrospinning AgNPs/PVA@Ag nanofibers substrate on a curved surface was carried out to detect the complicated mixture of Sudan I, CV and MG. These results demonstrate the aligned AgNPs/PVA@Ag nanofibers flexible SERS sensor will further be widely used in biochemical sensing applications.

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