

In situ* GENERATION OF Ag NANOPARTICLES ON POLY(VINYL ALCOHOL)/CHITOSAN NANOFIBERS AS FLEXIBLE SUBSTRATES FOR SURFACE-ENHANCED RAMAN SPECTROSCOPY DETECTION***Ying Chen^{1,2}, Jilin Cao^{1*}, Hengyong Wei^{3*}, Zhengang Wu⁴, Yingna Wei³**

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Flexible surface-enhanced Raman spectroscopy (SERS) substrates were produced by *in situ* chemical reduction of Ag⁺ on poly(vinyl alcohol)/chitosan (PVA/CS) nanofibers. PVA/CS nanofibers (which have a large number of amino and hydroxyl functional groups) were prepared by electrospinning, which can provide more sites for adsorbing Ag⁺ than pure PVA. The Ag nanoparticles were evenly distributed on the PVA/CS nanofibers. The SERS substrate also exhibited excellent water stability, sensitivity, and uniformity. The detection limit of probe molecule rhodamine 6G was 10⁻⁷ M and the relative standard deviation was 5%. In addition, the Ag-PVA/CS nanofibers substrate was effective for recognition and detection of norfloxacin, a well-known antibiotic that is pertinent to food safety and animal/human health.

Keywords: surface-enhanced Raman spectroscopy substrate, Ag nanoparticle, nanofiber, norfloxacin detection.

In situ* ГЕНЕРАЦИЯ НАНОЧАСТИЦ СЕРЕБРА НА НАНОВОЛОКНАХ ПОЛИВИНИЛОВЫЙ СПИРТ/ХИТОЗАН В КАЧЕСТВЕ ГИБКИХ ПОДЛОЖЕК ДЛЯ ОБНАРУЖЕНИЯ УСИЛЕНИЯ СИГНАЛОВ ГИГАНТСКОГО КОМБИНАЦИОННОГО РАССЕЯНИЯ*Y. Chen^{1,2}, J. Cao^{1*}, H. Wei^{3*}, Z. Wu⁴, Y. Wei³**

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Гибкие подложки для спектроскопии поверхностно-усиленного комбинационного рассеяния света (SERS) получены химическим восстановлением Ag⁺ *in situ* на нановолокнах поливиниловый спирт/хитозан (ПВС/ХС). Нановолокна ПВС/ХС с большим количеством амино- и гидроксильных функциональных групп получены методом электроформования, который может обеспечить больше мест для адсорбции Ag⁺, чем чистый ПВС. Наночастицы Ag равномерно распределены на наново-

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локнах ПВС/ХС. SERS-подложки демонстрируют высокие водостойкость, чувствительность и однородность. Предел обнаружения молекулы-зонда родамина 6G 10^{-7} М, относительное стандартное отклонение 5 %. Показано, что подложки на основе нановолокон Ag-ПВС/ХС эффективны для распознавания и обнаружения норфлоксацина — антибиотика, который имеет отношение к безопасности пищевых продуктов и здоровью человека и животных.

Ключевые слова: субстрат SERS, наночастица Ag, нановолокно, обнаружение норфлоксацина.

Introduction. Surface-enhanced Raman spectroscopy (SERS) exhibits excellent sensitivity and unambiguous recognition capabilities and has been widely applied to biology, food and environmental safety, and medicine [1–4]. To date, many approaches to fabricating SERS substrates have been suggested. Traditionally, such substrates are fabricated by depositing nanoparticles (NPs) onto rigid materials such as silicon, metal, and glass [5, 6]. However, these rigid substrates cannot be used for in situ analyses of samples from the field as they are fragile and inflexible. Furthermore, NPs are usually difficult to disperse homogeneously onto substrates, resulting in locally high-concentration regions, such as in the coffee-ring effect [7]. In contrast, flexible SERS substrates are practical in that they can exhibit uniform coverage and good mechanical flexibility, and can be swabbed onto a variety of surfaces for Raman-based detection [8–10].

Construction of composite SERS substrates by modification of plasmon nanostructures onto flexible supports (e.g., paper and polymer films) has been investigated [11, 12]. Electrospun nanofibers are a versatile, flexible substrate because they exhibit exceptional properties such as low diameter, high specific surface area, and a three-dimensional structure [13]. Various polymers [such as poly(styrene-co-butadiene), poly(vinyl alcohol) (PVA), polystyrene, polyvinylidene fluoride, polyamide, and polyimide] have been prepared to produce nanofibers by electrospinning for supporting SERS-active NPs [14–19]. Mixed electrospinning of two or three polymers with corresponding functional groups is also an active area of research that can reduce the time required for preparing nanofibers. Liu et al. reported that positively charged Au NPs could be immobilized onto poly(vinyl alcohol) PVA/poly(acrylic acid) (COO^-) electrospun nanofibers through electrostatic interactions. This fabrication method can avoid multistep procedures and also exhibits excellent SERS performance [20].

Poly(vinyl alcohol) is a water-soluble, biocompatible polymer; and exhibits high spinnability [21, 22]. It is commonly used in two-component electrospinning. To decorate Ag NPs uniformly onto the surface of PVA nanofibers and create hot spots, chitosan (CS) is used as a polymer auxiliary. CS is a natural polymer that is produced by deacetylation of chitin. It is a promising host matrix for controlled release, antibacterial agents, and biodegradation sensors [23, 24]. There are a large number of reactive functional groups [amino ($-\text{NH}_2$) and hydroxyl ($-\text{OH}$)] in the CS molecular chain that not only facilitate immobilization of Ag NPs but also exhibit high chemical affinity to various analytes [25, 26]. In general, much research has been reported on PVA/CS electrospun nanofibers that are composited with Ag NPs [27–29]. However, the focus of research has mainly been on the antibacterial and wound-healing activity of these materials.

A facile approach to immobilizing Ag NPs onto PVA/CS electrospun nanofibers for SERS-based detection is reported. The Ag^+ ions were anchored onto the electrospun nanofibers by chelation with $-\text{NH}_2$ and $-\text{OH}$. The Ag-PVA/CS nanofiber SERS substrates exhibited excellent sensitivity and uniformity. It was also used to detect and recognize norfloxacin.

Experimental. PVA (99% hydrolyzed, $\text{DP}=1700$), CS ($\text{Mw}=70000$, $\text{DD}\geq 95\%$), ascorbic acid (AR, 98.0%), silver nitrate (AgNO_3 , AR), rhodamine 6G (R6G, AR), acetic acid (AR, 99.5%), and norfloxacin (AR, 98.0%), were purchased from Shanghai Aladdin Reagent Co., Ltd. (China).

Preparation of PVA/CS electrospun nanofibers. CS was dissolved in 10 mL of 5 v/v% acetic acid and 4.8 g PVA was dissolved in 50 mL water under magnetic stirring for 2 h. The PVA and CS solutions were mixed at weight ratios of 16:1, 24:1, and 32:1, respectively. The mixture (10 mL) was loaded into a syringe with a 22-gauge blunt tip needle. Then, the syringe was driven by an electric syringe pump set at a fixed flow rate of 1 mL/h. The needle was connected to a high-voltage power supply (applied voltage: 25 kV). The nanofibers were collected with tin foil (receiving distance: 15 cm). The PVA/CS electrospun nanofibers were dried in an oven at 60°C.

Preparation of Ag-PVA/CS SERS substrates. To produce water-stable membranes, the PVA/CS nanofibers were crosslinked upon heat treatment at 160°C for 30 min. Then, the PVA/CS nanofibers (effective size 10×10 mm) were immersed in various concentrations of AgNO_3 and shaken gently for 30 min; subsequently, a corresponding quantity of ascorbic acid was added, and the Ag^+ was reduced to Ag NPs that were appended onto the nanofibers.

Field-emission scanning electron microscopy (SEM; S-4800; Hitachi, Japan) was used to visualize the morphology of the nanofibers (operating voltage: 10 kV). Energy-dispersive X-ray spectroscopy (NORAN; Thermo Fisher, USA) was used to analyze the elemental composition. Transmission electron microscopy (TEM; JEM-2800; Japan) at an operation voltage of 200 kV was used to observe the nanofibers. Attenuated total reflection–Fourier-transform infrared (FTIR) spectra of the nanofibers were recorded between 600 and 4000 cm^{-1} with a Bruker vertex 70 infrared spectrometer (Germany). The X-ray diffraction (XRD, D/MAX2500PC, Rigaku, Japan) was used to characterize the structural properties of the nanofibers.

R6G was selected as the SERS probe molecule and was dissolved in water at various concentrations (10^{-2} to 10^{-7} M). The R6G solutions were dripped onto the SERS substrates to measure the SERS activity of the AgNPs-PVA/CS nanofiber substrates.

Norfloxacin was dissolved in water with a small quantity of acetic acid and diluted to various concentrations (10^{-2} to 10^{-5} M). The norfloxacin solutions were dripped onto the SERS substrates. After evaporation of the water, the substrates were subjected to SERS measurements.

A laser Raman spectrometer [DXR, Thermo Fisher, USA; equipped with a 633-nm laser (1 mW at room temperature), an objective lens of $\times 10$, and laser spot diameter of 2.5 μm] was used to evaluate the SERS performance. The Raman integral time for collecting each spectrum was 5 s, with two accumulations by the laser confocal mode. The average power density of the laser radiation was $1.6 \times 10^4 \text{ W/cm}^2$.

Results and discussion. *Properties of PVA/CS nanofibers.* Figure 1 shows the procedure used to prepare the Ag-PVA/CS nanofibers. The PVA/CS nanofibers were first fabricated via electrospinning of a mixture of PVA and CS, then crosslinked by heat treatment to attain water stability.

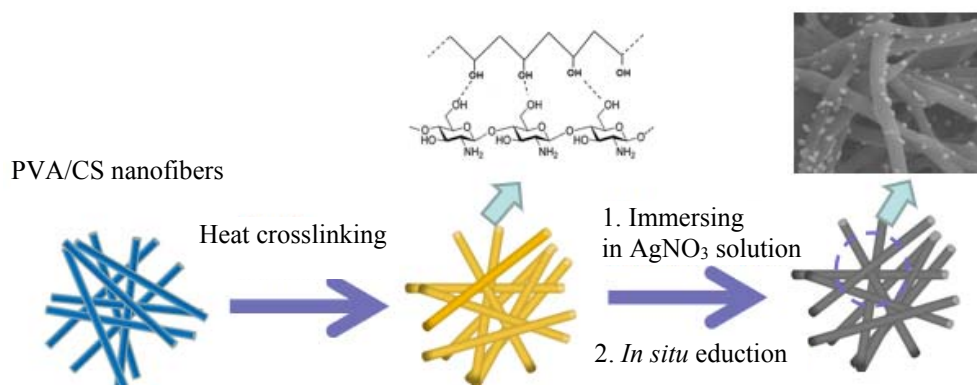


Fig. 1. Schematic of Ag NPs immobilization on PVA/CS nanofibers.

The PVA/CS nanofibers were observed by SEM (Fig. 2). PVA/CS (16:1) nanofibers were discontinuous and the diameter distribution was uneven (Fig. 2a). The electrospinning solution viscosity impacted the nanofiber morphology. If the solution were highly viscous, the spinneret might easily block and lead to unstable spinning. However, PVA/CS (24:1) nanofibers exhibited a uniform morphology, smooth surface, and random distribution (Fig. 2b). The inset of Fig. 2b shows a histogram of the PVA/CS nanofiber diameter distribution. Approximately 70% of the nanofibers were within 300–400 nm in diameter. However, increasing the ratio of PVA/CS (32:1) led to a large distribution of the nanofiber diameter (Fig. 2c). To apply PVA/CS nanofibers in SERS, as many Ag NPs as possible should be appended onto the resulting nanofibers; thus, PVA/CS (24:1) nanofibers were chosen. Figure 2d shows the morphology of the PVA/CS nanofibers after exposure to water for 1 h; the nanofibers were dissolved. As indicated by the inset of Fig. 2d, the nanofibers became transparent. That is because both the PVA and the CS are hydrophilic. Water molecules quickly entered into the nanofibers because of the large specific surface area and porosity, and the three-dimensional structure was no longer evident. Therefore, to produce water-stable membranes, the PVA/CS nanofibers were crosslinked upon heat treatment. After the heating treatment (Fig. 2e), PVA/CS nanofibers that exhibited water stability maintained their uniform and excellent porous fibrous morphology after exposure to water for 1 h, but the color of the PVA/CS nanofibers changed to light yellow. The rearrangement of molecular segments can be accelerated under heat treatment and thereby improve the crystallinity, which changes the physical properties of the polymer [30].

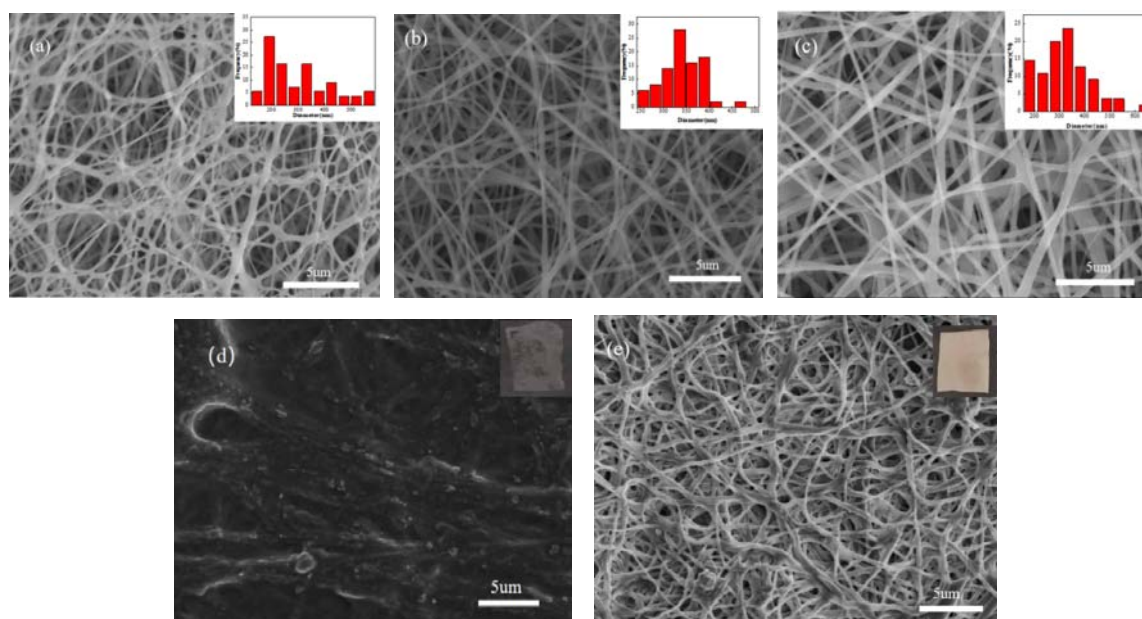


Fig. 2. SEM images of PVA/CS nanofibers of various weight ratios: (a) 16:1, (b) 24:1, and (c) 32:1; insets indicate the nanofiber size distribution histograms. SEM images of PVA/CS nanofibers after exposure to water (d) before heat crosslinking, and (e) after heat crosslinking; insets are corresponding optical images.

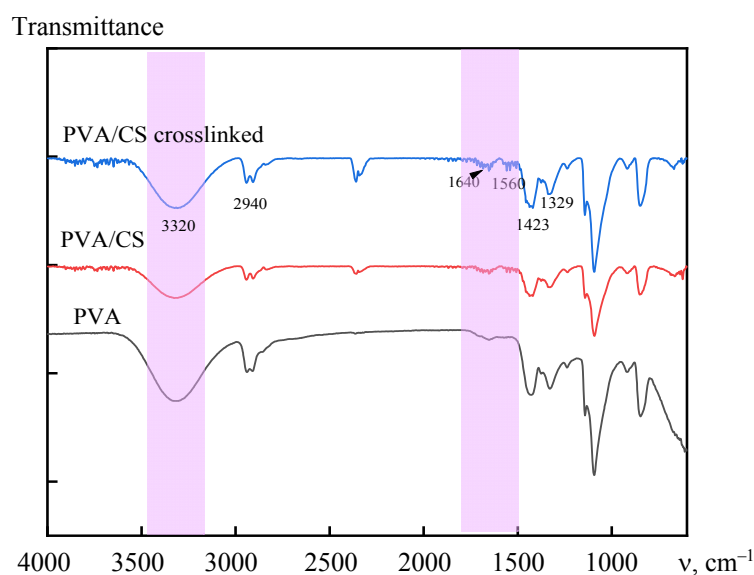


Fig. 3. FTIR spectra of PVA nanofibers and PVA/CS nanofibers before and after heat-crosslinking.

To investigate the chemical interactions between the PVA/CS nanofibers, attenuated total reflection-FTIR spectra were obtained (Fig. 3). The absorption peaks at 3320, 2940, 1423, and 1093 cm^{-1} were attributed to stretching vibrations of O-H, CH_2 , CH-OH, and C-O respectively in pure PVA; and they were also well-preserved in the PVA/CS nanofibers [31]. The absorption peak of the residual -COO group of PVA was evident near 1700 cm^{-1} , whereas the absorption peaks of the CS nanofibers at 1560 and 1640 cm^{-1} are attributable to the bending vibrations of the amide groups [29, 32].

Because of the low content of CS and the hydrogen bonds between the $-\text{NH}_2$ group of CS and the $-\text{OH}$ group of PVA, strong peaks were not observed in the PVA/CS nanofibers. The FTIR spectra of the PVA/CS nanofibers after heat crosslinking exhibited little change. Thus, the Ag^+ ions anchor onto the surface of the PVA/CS nanofibers after heat crosslinking by the chelating effect of abundant NH_2 and OH groups, and then generate Ag NPs by in situ reduction with ascorbic acid.

Characterization of Ag-PVA/CS nanofibers. The AgNO_3 concentration substantially affected the distribution of the Ag NPs, which directly corresponded to the SERS activity. Figures 4a–c show SEM images of Ag-PVA/CS nanofibers in various concentrations of AgNO_3 (0.001, 0.005, and 0.01 M). The quantity of Ag NPs on the nanofiber surface increased gradually with increasing concentration of Ag^+ . A few Ag NPs were observed on the nanofiber surface in Fig. 4a; here, the concentration of AgNO_3 was 0.001 M. Figure 4b indicates that the nanofibers were modified more uniformly with Ag NPs at a concentration of 0.005 M, which resulted in creation of more SERS hot spots. However, when the concentration of AgNO_3 reached 0.01 M, the growth of Ag NPs on the nanofiber surface was substantially increased, resulting in uneven distribution and aggregation (Fig. 4c). The hot spots between the Ag NPs may be destroyed because of the aggregation, which affects the performance of SERS. Therefore, 0.005 M was chosen as the optimal concentration of AgNO_3 for the experiments. Figure 4e–g shows EDS elemental mapping images of N, Ag, and C on the Ag-PVA/CS nanofibers optimized at an AgNO_3 concentration of 0.005 M. The Ag NPs were uniformly distributed on the nanofibers and the PVA and CS were also finely mixed. Moreover, on the TEM images, there were uniform spherical Ag NPs on the surface of the PVA/CS nanofibers (Fig. 4d). The inset of the high-resolution TEM image of Fig. 4d indicates an interplanar spacing of 2.37 Å, corresponding to the lattice spacing of the (111) planes of the Ag face-centered cubic facet [33].

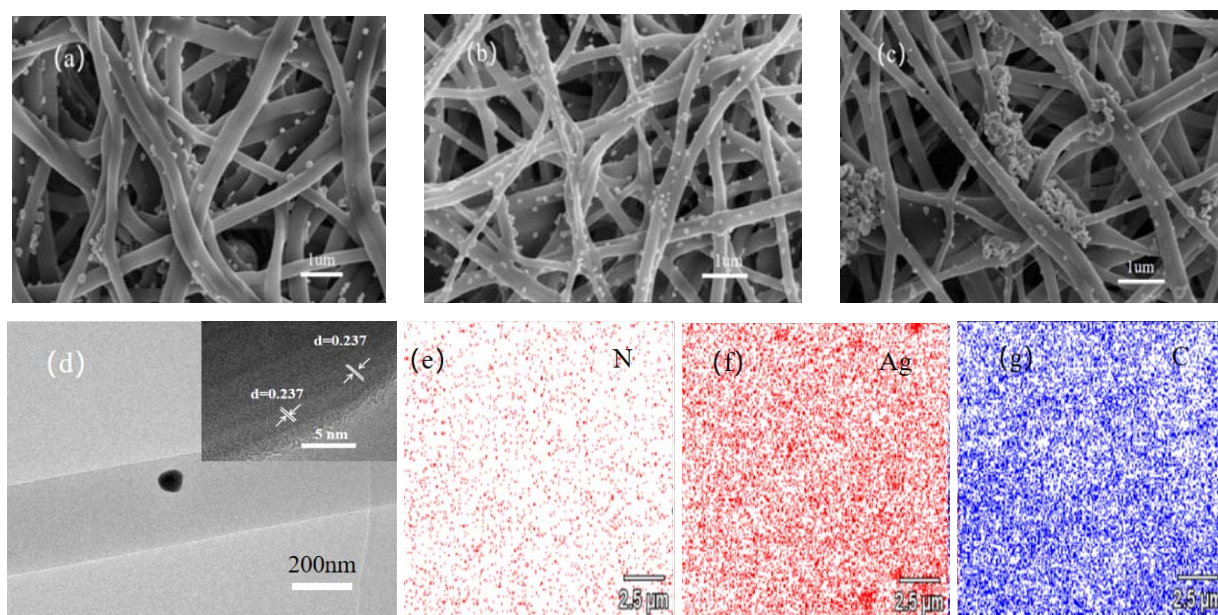


Fig. 4. SEM images of Ag-PVA/CS nanofibers at various AgNO_3 concentrations: (a) 0.001 M, (b) 0.005 M, and (c) 0.01 M; (d) TEM image of Ag-PVA/CS; and (e)–(g) corresponding EDS elemental mapping of Ag-PVA/CS.

Figure 5 shows XRD patterns of the PVA/CS nanofiber substrate and Ag-PVA/CS nanofiber substrate. The samples both exhibited a broad diffraction peak between 17° and 23° , corresponding to the (101) plane of the PVA semicrystalline structure [34]. The XRD patterns of the Ag-PVA/CS nanofiber substrate corresponded to the XRD peaks at 2θ of 38.66° , 44.42° , 64.22° , and 77.16° , which result from the typical face-centered cubic crystalline structure of metallic silver at (111), (200), (220), and (311), respectively [35]. These results are also indicative of Ag NP immobilization on the surface of the PVA/CS nanofibers.

SERS performance of the substrates. R6G was used as a probe to evaluate the performance of the Ag-PVA/CS nanofiber substrates. A drop of R6G solution ($50\ \mu\text{L}$) was added onto the SERS substrate ($10\times 10\ \text{mm}$). Upon drying the substrates, the Raman spectra were collected. Figure 6a indicates that R6G ($10^{-2}\ \text{M}$) did not correspond to a notable Raman spectrum on the PVA/CS substrate without Ag NPs, which also indicates that the substrate did not interfere with detection. In comparison, R6G ($10^{-2}\ \text{M}$) exhibited substantial Raman enhancement on the Ag-PVA/CS nanofiber substrate; the Raman characteristic peaks at $610\ \text{cm}^{-1}$ (C–C–C ring in-plane bending), 769 and $1362\ \text{cm}^{-1}$ (C–H bending), and 1512 and $1650\ \text{cm}^{-1}$ (C–C bond stretching) were readily distinguished [36]. Here, when the Ag NPs were excited with a laser, a hot spots effect was generated that enhanced the local electromagnetic fields and increased the SERS signals.

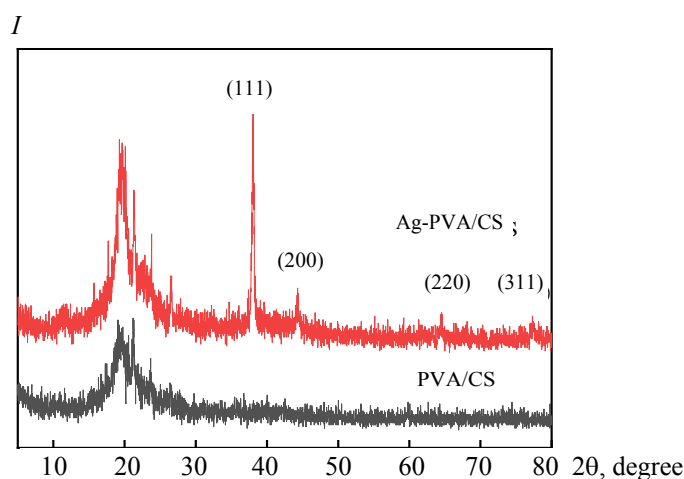


Fig. 5. XRD patterns of PVA/CS nanofibers and Ag-PVA/CS nanofibers.

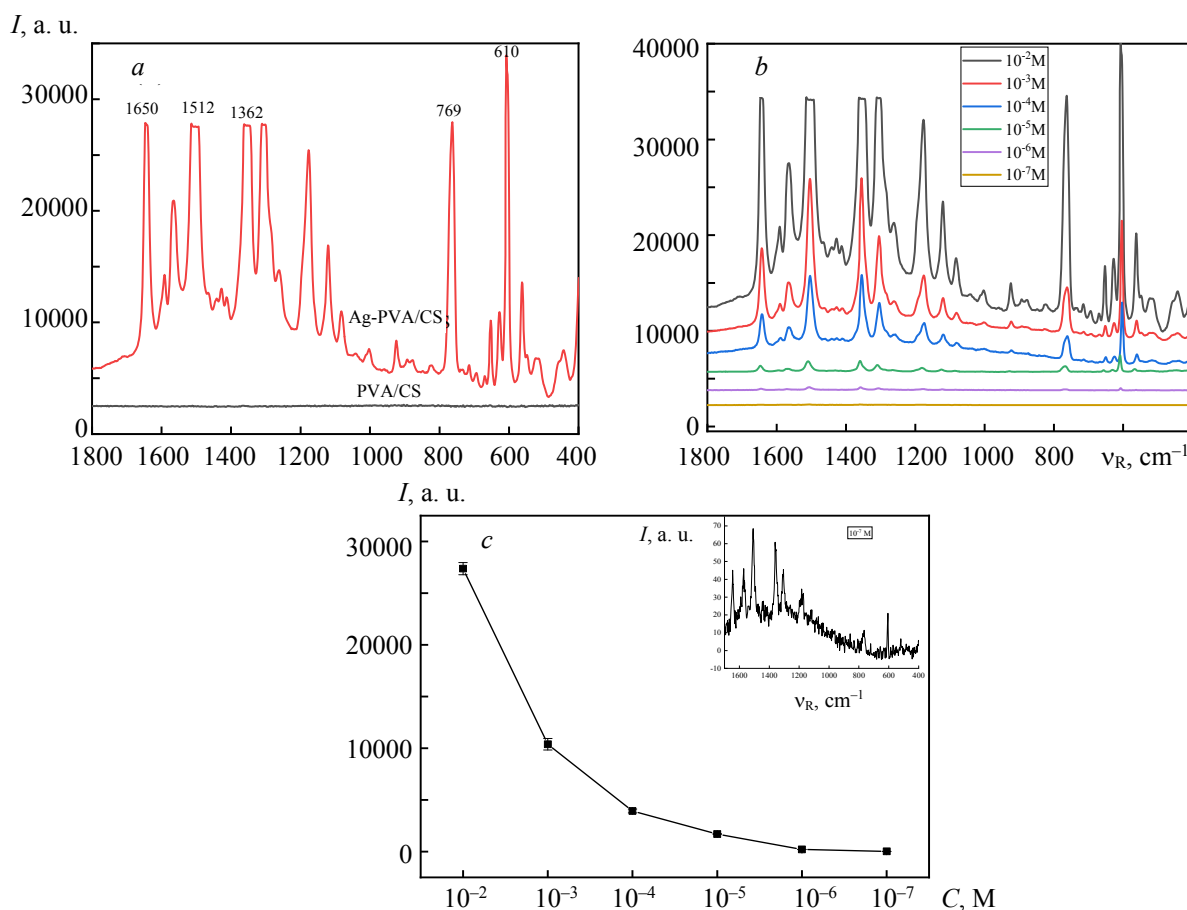


Fig. 6. (a) Raman spectra of 10^{-2} M R6G on various substrates, (b) SERS spectra of R6G at concentrations from 10^{-2} to 10^{-7} M, and (c) relationship between the SERS intensity at 610 cm^{-1} and various concentrations of R6G.

To further evaluate the SERS ability of the Ag-PVA/CS nanofiber substrates, SERS spectra of R6G at various concentrations were measured. A drop of aqueous R6G (10^{-2} to 10^{-7} M) was added onto the Ag-PVA/CS substrates. Figure 6b shows the SERS spectra of R6G. Peaks were evident for all of the substrates,

although the intensity weakened with decreasing concentration. Figure 6c shows the Raman peak intensity at 610 cm^{-1} versus the concentration of R6G. The intensity of the peak at 610 cm^{-1} decreased as the concentration of R6G decreased from 10^{-2} to 10^{-7} M ; the SERS peaks were still distinguishable when the concentration reached 10^{-7} M . The Ag-PVA/CS nanofiber substrates provided not only abundant hot spots that produced electromagnetic enhancement but also a large surface area for the absorption of probe molecules.

Additionally, the enhancement factor (EF) was calculated using the equation: $EF = (I_{\text{SERS}}/I_{\text{R}})/(C_{\text{SERS}}/C_{\text{R}})$ [37], where I_{SERS} and I_{R} are the Raman signal intensities of the SERS and nor-mal substrates, respectively; and C_{SERS} and C_{Raman} are the concentrations of the analyte on the SERS (10^{-7} M) and unmodified (10^{-1} M) substrates, respectively; $EF = 1.86 \times 10^6$ for the case of R6G at 610 cm^{-1} . The uniformity of the SERS signals is important for the practical analysis of molecules. To evaluate the SERS signal uniformity of the substrate, R6G (10^{-2} M) absorbed onto the substrate was measured. The uniformity of the Raman signals was illustrated by collecting SERS spectra from 20 random positions of the Ag-PVA/CS substrate (Fig. 7a). The peaks and shape of the SERS signals were fairly consistent. The variations in the prominent peak intensity at 610 cm^{-1} exhibited a slight fluctuation with a relative standard deviation (RSD) of 5.00% (Fig. 7b), thus confirming excellent uniformity.

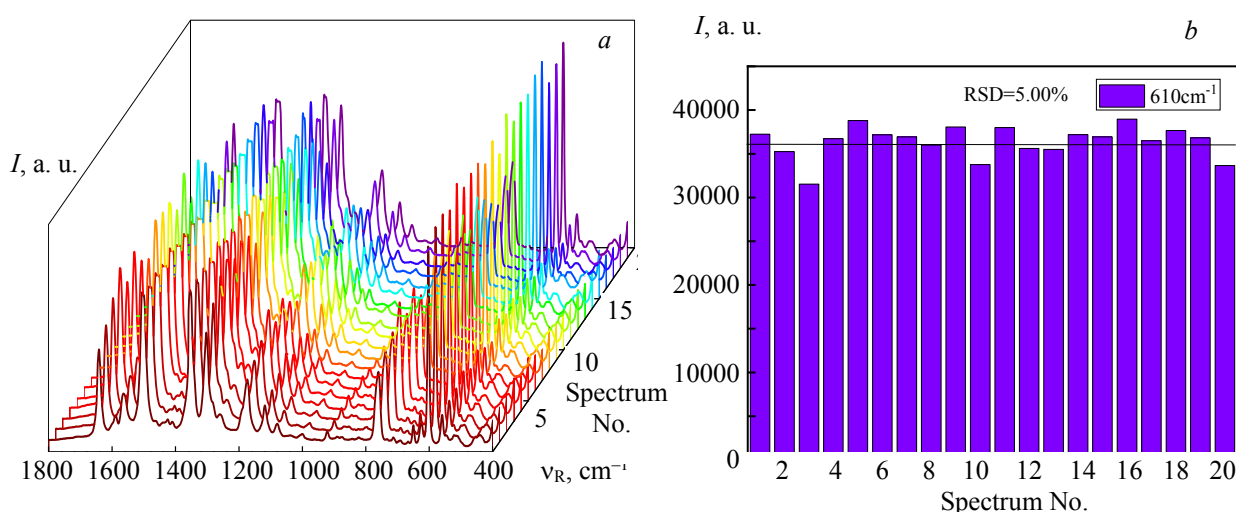


Fig. 7. (a) SERS spectra collected from 20 randomly selected positions of Ag-PVA/CS nanofibers, and (b) intensity of SERS signals at 610 cm^{-1} .

SERS detection of norfloxacin. To verify applicability of the substrates to detecting drug molecules, the as-prepared substrates were applied to detect norfloxacin. Norfloxacin is a typical antibacterial agent that is in the fluoroquinolone class of drugs [38]. Abuse of antibiotics substantially threatens food safety and may lead to environmental pollution and human health problems [39]. Therefore, it is necessary to identify and detect norfloxacin quickly in the field. Figure 8 shows the Raman spectrum of norfloxacin powder and the SERS spectra of norfloxacin solution (10^{-2} M) absorbed onto Ag-PVA/CS and PVA/CS substrates. The main vibrations were identified by the Raman spectra of fluoroquinolones reported in the literature, as follows: 703 and 746 cm^{-1} , quinoline ring breathing vibration; 1294 cm^{-1} , stretching vibration of C–N; 1393 cm^{-1} , asymmetric vibration of O–C–O; 1469 and 1541 cm^{-1} , quinoline ring deformation vibration; and 1622 cm^{-1} , stretching vibration of C=C [40, 41]. The primary characteristic peaks in the SERS spectrum were detected with some minor differences, which may be because of different adsorbed orientations and sites of the norfloxacin molecules on the substrate [42]. In contrast, there was no signal of norfloxacin (10^{-2} M) on a pure PVA/CS substrate.

Figure 9a shows the SERS spectra of norfloxacin at various concentrations (10^{-2} to 10^{-5} M). With decreasing concentration, the intensities of the SERS signals decreased gradually. When the concentration of norfloxacin was as low as 10^{-5} M , the characteristic peaks were still clearly identified. There was a good linear relationship ($R^2 = 0.924$) between the logarithmic concentration of norfloxacin and the logarithmic peak intensity at 1393 cm^{-1} (Fig. 9b). Thus, Ag-PVA/CS substrates are promising platforms for detecting drug molecules by SERS.

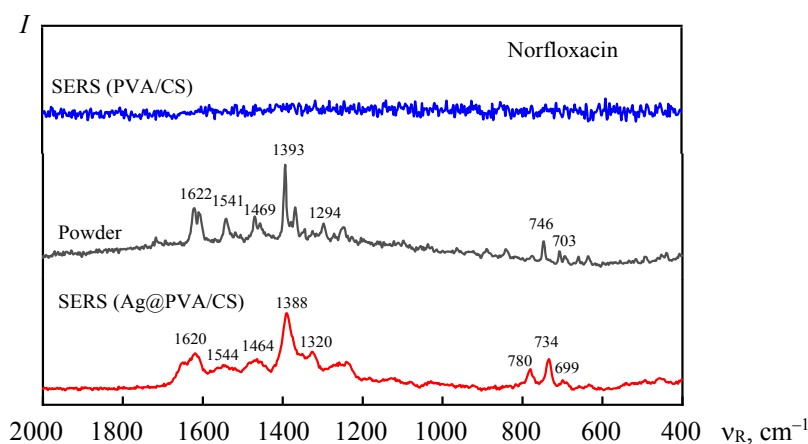


Fig. 8. Raman spectra of norfloxacin powder, and norfloxacin solution (10^{-2} M) on Ag-PVA/CS and PVA/CS.

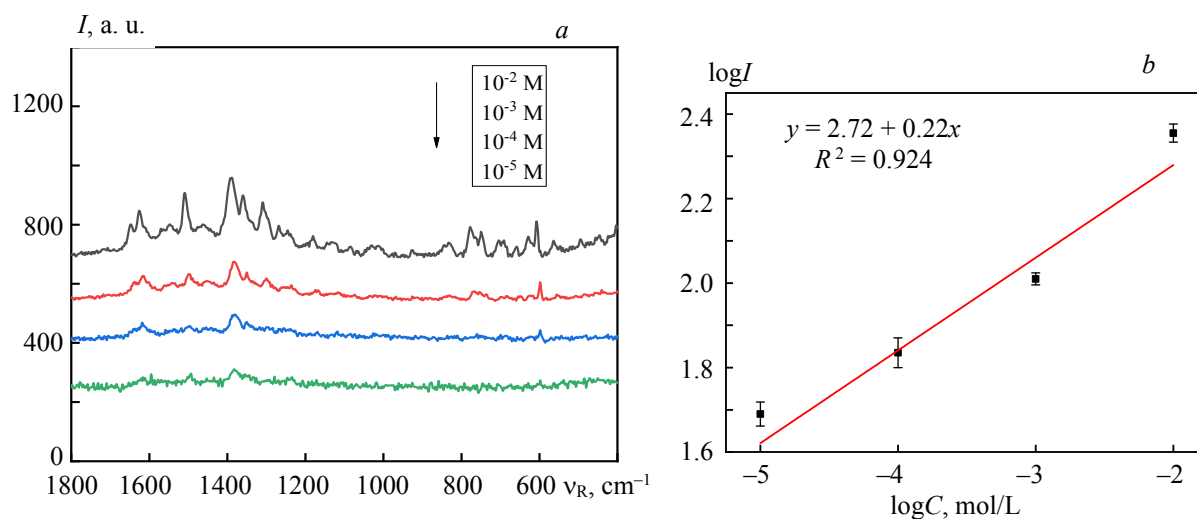


Fig. 9. (a) SERS spectra of norfloxacin at various concentrations, and (b) plot of the 1393 cm^{-1} $\log I$ versus $\log C$ of norfloxacin.

TABLE 1. Comparison of the LOD and RSD of Reported SERS Substrates

SERS material	Analyte	LOD, M	RSD, %	Ref.
Au-PVA nanofibers	DTTCI (3,3'-diethylthi-atricarbocyanine iodide)	10^{-7}	10	[14]
Ag/SB (Styrene-butadiene) nanofibers	R6G Triazophos	10^{-9} 10^{-8}	8.12	[15]
Ag-PI (Polyimide) nanofabrics	p-ATP (adenosine triphosphate)	10^{-14}	<20	[19]
Au-CS/PEO [Poly(ethylene oxide)]nanofibers	2-Naphthalenethiol R6G	10^{-15} μM	/	[43]
Ag-PVA/CS nanofibers	R6G Norfloxacin	10^{-7} 10^{-5}	5	This study

In addition, the results during the present study on SERS were compared with the results of work where other electrospinning nanofibers were used, including the probe molecules used and the limit of detection (LOD) and RSD achieved in Table 1. Although the LOD achieved was similar to or not as low as in the literature, some of the materials (Au) used to prepare SERS substrates in the literature are more expensive than those used in the present work, and some of the electrospinning solvents (e.g., dimethylformamide) are toxic. In the present study, the PVA/CS nanofibers can be prepared in a straightforward and environmentally friendly manner, and the RSD exhibited reasonable uniformity.

Conclusions. Ag nanoparticles were loaded onto the surface of heat-crosslinked PVA/CS nanofibers by *in situ* reduction, which can form more hot spots. The SERS performance of the substrates was evaluated by using R6G as a probe. The Ag-PVA/CS nanofibers exhibited high sensitivity with an LOD of 10^{-7} M for R6G. The as-prepared SERS substrates were also applied to detecting norfloxacin. Hence, the Ag-PVA/CS nanofibers substrate has great potential in sensitive, *in situ*, and onsite detection of drug molecules.

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