Preparation of Ag@PDA@SiO$_2$ electrospinning nanofibrous membranes for direct bacteria SERS detection and antimicrobial activities

Menghui Wan$^1$, Haodong Zhao$^1$, Zhihua Wang$^{2,*}$, Yanbao Zhao$^1$ and Lei Sun$^{1,*}$

$^1$ Engineering Research Center for Nanomaterials, Henan University, Kaifeng 475004, People’s Republic of China
$^2$ Henan Engineering Research Center of Industrial Circulating Water Treatment, College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, People’s Republic of China

* Authors to whom any correspondence should be addressed.
E-mail: zhwang@henu.edu.cn and sunlei@henu.edu.cn

Keywords: electrospinning, SiO$_2$ nanofibers, Ag nanoparticles, SERS, bacteria detection

Abstract

In this paper, a convenient method to fabricate flexible and free-standing surface-enhanced Raman scattering (SERS) substrates for direct bacteria detection without aptamer bonding is presented. SiO$_2$ nanofibers were prepared via electrospinning and calcination by using tetraethyl orthosilicate as the precursor. Subsequently, it was coated with polydopamine (PDA) by self-polymerization. Finally, Ag@PDA@SiO$_2$ nanofibrous membranes were obtained through in situ growth of Ag nanoparticles in Tollens’ reagents. The as-prepared Ag@PDA@SiO$_2$ composite nanofibrous membranes were characterized by techniques of scanning electron microscopy, transmission electron microscopy, X-ray powder diffraction, energy-dispersive x-ray spectroscopy and thermo gravimetric analysis. The flexibility of the as-prepared nanofibrous membranes were verified simply through manual folding. Small molecule probes of 4-mercaptophenol (4-MPh) and 4-mercaptobenzoic acid (4-MBA) were chosen to investigate the SERS sensitivity of the as-prepared Ag@PDA@SiO$_2$ as free-standing substrates. Furthermore, *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*), as typical strains of Gram-negative and Gram-positive bacteria, were performed to directly SERS detection by dropping bacteria suspension onto the fibrous membranes without any previous treatment, such as aptamer combination. In addition, the antimicrobial properties of the as-prepared Ag@PDA@SiO$_2$ electrospinning nanofibrous membranes were tested by inhibition zone and turbidity methods. The results show that Ag nanoparticles with an average diameter of 50 nm are uniformly deposited on the surface of electrospinning nanofibers, and the as-prepared Ag@PDA@SiO$_2$ nanofibrous membranes are flexible. As SERS substrates, it shows a rather high detection limitation of $10^{-11}$ mol l$^{-1}$ for 4-MPh and 4-MBA. More importantly, this substrate can be applied for bacteria label-free SERS detection, i.e., complicated procedures are avoided. Meanwhile, the as-prepared Ag@PDA@SiO$_2$ nanofibrous membranes exhibit excellent antibacterial properties. Thus, it has application prospects in trace bacteria detection and water purification.

1. Introduction

The threaten of pathogenic bacterium to public safety and human health has become a serious social concern, since the abuse of antibiotic in some countries and regions, which results in the propagation of drug-resistance bacteria [1]. Therefore, in order to prevent the occurrence of bacterial diseases, it is of great significance to investigate high-efficiency and broad-spectrum, low drug-resistance antibacterial materials, as well as rapid and sensitive detection techniques for pathogenic bacteria [2–6]. To answer this concern, much efforts have been
made to develop nanomaterials with antibacterial activity. Among of them, nano-silver has achieved great attention owing to its high antimicrobial activities, low toxicity to normal cells, good thermal stability. Moreover, the noble metal silver nanostructures exhibit excellent surface-enhanced Raman scattering (SERS) activity due to its strong localized surface plasmon resonance characteristics, and are usually served as SERS substrates for detection and analysis [7−9]. SERS technique is also be applied to bacteria detection, since most of bacteria exhibit its unique and characteristic Raman signals [10]. It possesses some advantages such as high sensitivity, non-destructive, rapid, enabling micro-detection, and can provide molecular structural information from germs [11]. Therefore, the technique is widely used in biomedical analysis, disease diagnosis, and food safety testing [12], etc. For example, Yuan et al have reported the enrichment of bacteria by magnetic separation and modification to stable Au@Ag−GO nanocomposite with SERS tags, and various pathogens were detected, accompanied with good antibacterial properties [13]. Gao et al have reported that SERS detection was performed by combining aptamer-modified Ag nanoparticles with bacteria, and the detection sensitivity was up to 1.5 colony-forming units (cfu)/ml [11]. Zhang et al have prepared Au nanoparticles with specific recognition of aptamer modification for detection of Staphylococcus aureus and Salmonella typhi [14]. Although the above detection of pathogenic bacteria is sensitive and specific, all of them are involved aptamer or probe molecules labeling. Since the label modification procedure is very time consuming, and the operation is rather complicated, this bacteria detection method with label is imperfect. Therefore, it is necessary to develop a direct, efficient, in situ method for obtaining bacterial intrinsic Raman fingerprints [15]. Although noble metal of nano-silver has strong SERS performance and inherent antibacterial properties [16], it is still challenging to prevent the formation of aggregates, and to control size [17, 18]. Thus, it is of practical research significance to fabricate suitable support materials as SERS substrates, simultaneously, control the aggregation of nanoparticles, enhance Raman effect and antibacterial properties [19, 20].

Electrospinning is a method that can produce flexible, self-supporting nanofibrous membranes directly and continuously, furthermore, it has other advantages, such as controllability, low-cost equipment [21, 22]. These membranes are ideal carriers for nanoparticles due to their large specific surface area, high porosity and good mechanical properties. The composite nanofibrous membranes incorporated with silver nanoparticles exhibit wide applications in biosensing, SERS, catalysis [23−25]. For example, Fu et al have prepared polydopamine functionalized silver-plated SiO2 nanofibers, and demonstrated that the samples have good electrical conductivity [26]. Zhang et al prepared a highly sensitive SERS substrate by aminating the surface of polycrylonitrile fibers, and then depositing Ag nanoparticles on the surface of the fibers through in situ seed growth method [20]. Our group has prepared TiO2−Ag composite nanofibrous membranes, which exhibit a rather high SERS detection sensitivity and excellent antibacterial activities [27]. Although the most electrospinning fibers are formed with polymers, inorganic materials, such as SiO2 nanofibers, have also attracted attention for its physicochemical stability and mechanical strength. It is reported that SiO2 electrospinning nanofibers exhibit good thermal stability, large specific surface area, good flexibility and biocompatibility [28, 29]. Simultaneously, SiO2 nanofibers are convenient for combination with other materials, safe and non-toxic [30, 31]. What’s more, SiO2 nanofibrous membranes don’t show any intrinsic Raman signals in SERS detection, compared with other substrate, e.g. TiO2 [32]. Thus, SiO2 electrospinning nanofibrous membranes are considered ideal carrier materials for SERS substrates fabrication.

Polydopamine (PDA) structure is like the adhesion protein secreted by mussels. Dopamine can be oxidized and self-polymerized into PDA, which adheres almost spontaneously to the surface of various substrates [33]. More importantly, PDA molecule contains a large amount of phenolic hydroxyl and amino groups, which can provide a large number of anchoring sites for metal ions and combine with them, promote the in situ formed nanoparticles incorporate rigidly with the surface of substrate [34, 35].

Based on the above reason, herein, a composite nanofibrous membrane was developed for labeling-free bacteria SERS detection and high antibacterial performance. First of all, SiO2 precursor nanofibers were prepared through electrospinning technique by using tetraethyl orthosilicate (TEOS) as raw materials. Subsequently, it was calcinated in an oven to obtain SiO2 nanofiber. And then, the as-prepared SiO2 nanofibrous membranes were surface modified by immersion in dopamine solution. At last, Ag nanoparticles incorporated into fibrous membranes were obtained via the reduction of AgNO3 by glucose. The final product was noted as Ag@PDA@SiO2 nanofibrous membranes for convenient description. The composition, morphology and structure of Ag@PDA@SiO2 nanofibrous membranes were characterized intensively by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), energy-dispersive x-ray spectroscopy (EDX), thermogravimetric analysis (TGA), etc. To investigate the SERS effect of the as-prepared Ag@PDA@SiO2 nanofibrous membranes, small molecule probes and bacteria were detected. Furthermore, its antibacterial properties were evaluated by methods of inhibition zone and turbidity. In brief, we present a flexible and free-standing SERS substrate with ultrahigh Raman enhancement activities for direct detection of bacteria without labeling, as well as excellent antibacterial properties.
2. Experimental

2.1. Chemicals and materials
Polyvinyl pyrrolidone (PVP, Mw = 1300 000), 4-mercaptophenol (4-MPh), 4-mercaptobenzoic acid (4-MBA), dopamine hydrochloride, tris (hydroxymethyl)-aminomethane (Tris) were supplied by Aladdin Biological Technology Co., Ltd (Shanghai, China). AgNO₃ was purchased from Sinopharm Chemical Reagent Co., Ltd (Beijing, China). Tetraethyl orthosilicate (TEOS), N, N-dimethyformamide (DMF), dimethyl sulfoxide (DMSO), ammonia solution (NH₄OH, 25~28%), hydrochloric acid (HCl), absolute ethanol (EtOH), and glucose were purchased from Kemiu Chemical Reagent Co., Ltd (Tianjin, China). All the above reagents are of analytical grade and used without further purification. Nutrient agar and broth medium were purchased from Aoboxing Biotechnology Corporation Biotechnology Co., Ltd (Beijing, China). Strains employed in the test, i.e., Gram-negative bacteria of Escherichia coli (E. coli, ATCC 25922) and Gram-positive bacteria of Staphylococcus aureus (S. aureus, ATCC 6538) were purchased from Guangdong Huankai Microbial Technology Co., Ltd (Guangzhou, China).

2.2. Instruments and characterization
The electrospinning equipment is assembled in our laboratory by high voltage power supply (Dalian Dingtong Technology Development Co., Ltd, DE-100, and 0–50 kV, China), microinjection pump (Baoding Lange Constant Flow Pump Co., Ltd, LSP02–1B, China) and an aluminum foil receiving device fixed on the cardboard. SEM images were taken by a field emission scanning electron microscope (FEI, Nova Nano SEM 450, US) with a maximum operating voltage of 30 kV, a spot size of 3.0 nm, and a working distance of 5 mm. EDX was acquired by an energy spectrum accessory (OXFORD, X-MaxN, UK) on a Zeiss Gemini 500 scanning electron microscopy (Germany). TEM images were collected using a transmission electron microscope (JEOL JEM-2100, Japan) at an acceleration voltage of 200 kV. XRD phase structure analysis pattern was performed on an x-ray diffractometer (BRUKER D8-ADVANCE, Germany) using copper Kα (λ = 1.5418) radiation, operating voltage and current were 40 kV and 40 mA, respectively. TGA data was obtained by a TAQ600 synchronous thermal analyzer (TA Instrument, US). Raman spectra were acquired at an excitation wavelength of 785 nm using a Renishaw RM-1000 laser confocal Raman spectrometer (UK).

2.3. Preparation of SiO₂ nanofibers through electrospinning
Firstly, 0.60 g PVP was added slowly into 3.25 g DMF and 0.65 g DMSO, and kept with stirring for 3 h at ambient temperature. And then, 0.80 g TEOS was mixed with 0.30 g HCl solution (3 drops of 6.0 mol l⁻¹ of hydrochloric acid added to 25 ml of distilled water) and 0.20 g ethanol under vigorous stirring for 10 h. Subsequently, the above solutions were mixed and magnetically stirred for 3 h to obtain the silica precursor solution. After that, the solution was placed in a 10 ml plastic syringe equipped with a 22-gauge stainless-steel needle, and sprayed at a feed rate of 0.8 ml h⁻¹. The distance from needle tip to collector aluminum plate was 15 cm and the applied voltage was kept at 16 kV. To prepare SiO₂ nanofibers, the precursor nanofibers were firstly calcined in a programmed heating tube furnace under air atmosphere at 200 °C for 2 h with a ramp rate of 1.5 °C min⁻¹. Subsequently, another calcination stage was carried out at a condition of 600 °C, 3 h and 3 °C min⁻¹.

2.4. Preparation of PDA@SiO₂ nanofibers
2 mg ml⁻¹ dopamine aqueous solution was formulated by dissolving dopamine hydrochloride in Tris-buffer (10 mmol l⁻¹) and adjusting pH of the solution to 8.5. And then, 10 mg of SiO₂ nanofiber mats were soaked directly into the dopamine solution and stirred for 24 h at room temperature. After reaction finished, the color of the solution changed from pink to dark brown and the membranes were washed with distilled water for several times. Finally, the as-obtained PDA@SiO₂ nanofibrous membranes were dried at 40 °C for 12 h in vacuum.

2.5. Preparation of Ag@PDA@SiO₂ nanofibers
Firstly, 250 mg AgNO₃ was dissolved in 50 ml distilled water, the concentration of AgNO₃ in this case is 5 mg ml⁻¹. And then, ammonia solution was dropped into the formulated AgNO₃ solution, the color of the solution changed from colorless to dark yellow, finally to colorless again. Subsequently, 10 mg PDA@SiO₂ nanofibrous membranes were immersed into the freshly prepared Tollens’ reagent under stirring for 0.5 h. After that, 5 ml glucose (10 mg ml⁻¹) was slowly added into the above mixed solution and stirred for 1 h. Lastly, the membranes were taken out, washed with distilled water for three times and dried in a vacuum oven at 40 °C for 6 h. To obtain a series samples, 3 mg ml⁻¹ and 10 mg ml⁻¹ AgNO₃ solution were also configured, and the concentration of glucose was twice that of AgNO₃ to formulate different Tollens’ reagent. Taking the same procedure, Ag@PDA@SiO₂ nanofibrous membranes were prepared with different deposition amount.
of Ag nanoparticles. They were marked as samples of Ag@PDA@SiO$_2$-3, Ag@PDA@SiO$_2$-5, and Ag@PDA@SiO$_2$-10, respectively.

2.6. SERS measurements for 4-MBA and 4-MPh

4-MBA and 4-MPh were selected as the model probe molecules for evaluating the SERS sensitivity. The as-prepared Ag@PDA@SiO$_2$ nanofibrous membranes were immersed into aqueous solutions of probe molecules with different concentrations for 2 h. After that, they were washed with ethanol for three times, and dried under ambient conditions. Finally, the Raman measurements equipped with a 785 nm He-Ne laser, 0.5 mW of laser intensity, 10 s of integration time, as well as a 50 $\times$ microscope objective were applied to the samples.

2.7. SERS measurements for bacteria

Briefly, 6 ml of the bacteria nutrient medium (10$^8$ cfu/ml) was cultured for 12 h, and centrifuged at 6000 r min$^{-1}$ for 5 min. The bacteria precipitate was obtained after the centrifugation was washed 3 times with 0.9% NaCl solution. And then, it was dispersed in 200 $\mu$l of 0.9% NaCl solution for the coming testing. 15 $\mu$l of bacteria suspension was dropped onto the surface of the Ag@PDA@SiO$_2$ nanofibrous membranes, and allowed to dry for 15 min before SERS detection. The Raman test was conducted at laser wavelength of 785 nm, 100 $\times$ microscope objective, exposure time of 10 s, laser power of 0.5 mW, and acquisition wavelength range of 300~1800 cm$^{-1}$.

2.8. Antimicrobial testing

The bacteriostatic of the as-prepared Ag@PDA@SiO$_2$ nanofibrous membranes were evaluated by inhibition zone and turbidity method.

The inhibition zone operation process is as follows: Firstly, 100 $\mu$l of the bacteria suspension was uniformly coated on a solidified agar plate, and then, a piece of 6 $\times$ 6 mm$^2$ membranes sample was sterilized for 5 h and put onto the surface of the agar. Finally, the culture dish was placed in a 37 °C incubator for 16 h, and the size of the inhibition zone was measured.

The antibacterial activity of the nanofibrous membranes was further tested by the turbidity (OD$_{600}$) method. Firstly, 5 mg of nanofibrous membranes and 40 $\mu$l bacteria suspension were injected into a 10 ml test tube with 4 ml of 0.9% NaCl solution to collect the bacteria. Subsequently, the absorbance of samples was determined at 600 nm through a 725N UV–vis spectrophotometer.

2.9. SEM observation of bacteria morphology

Micromorphology changes of bacteria before and after the interaction with Ag@PDA@SiO$_2$ nanofibrous membranes were observed through SEM for supposing of the possible antibacterial mechanism. Firstly, 40 $\mu$l of bacteria suspension was added in sterilized 2 ml broth medium and cultured in a rotary shaker at 120 r min$^{-1}$ for 6 h. Secondly, 5 mg Ag@PDA@SiO$_2$ nanofibrous membranes were added to the above medium and cultured for 6 h. In the contrast experiment, 40 $\mu$l of bacterial suspension were added to 4 ml broth and cultured in the shaker for 12 h. Next, two groups of bacteria suspensions were centrifuged at 6000 r min$^{-1}$ for 6 min and washed three times with phosphate buffer saline (PBS, pH = 7.4) solution to collect the bacteria. Subsequently, the bacteria were immersed into glutaraldehyde solution (2.5%) at 4 °C for 12 h, and centrifuged for 5 min at 5000 r min$^{-1}$. Finally, different concentrations of alcohol were applied to dehydrate, and the dehydrated bacteria were observed by SEM.

3. Results and discussion

3.1. Morphology and structure analysis of Ag@PDA@SiO$_2$ nanofibers

Figure 1 shows SEM images of nanofibers of SiO$_2$ precursor (a), SiO$_2$ (b), PDA@SiO$_2$ (c), Ag@PDA@SiO$_2$-3 (d), Ag@PDA@SiO$_2$-5 (e), and Ag@PDA@SiO$_2$-10 (f). As shown in figure 1(a), SiO$_2$ precursor nanofibers obtained before the calcination process exhibit a smooth surface and a uniform diameter distribution. Accordingly, the mean diameter of the nanofibers are counted to 586 ± 35 nm, as shown in figure S1(a) is available online at stacks.iop.org/MRX/7/095012/mmedia. In contrast, as shown in figure 1(b), SiO$_2$ nanofibers gained after calcination basically maintain a uniform morphology like the SiO$_2$ precursor nanofibers; the surfaces are smooth and flat without bending or breaking. However, it is clearly seen that the mean diameter of fibers decreases after calcination. Figure S1(b) shows that it is reduced to 390 ± 37 nm. The decrease in fibers diameter implies the removal of organic matters in the precursor nanofibers, such as PVP. As a result, the pure inorganic nanofibers of the amorphous SiO$_2$ are formed [36], and this phase structure can be verified by the following XRD analysis. It can be seen from figures 1(c) and S1(c) that there is no obvious change in fibers morphology and diameter size, except for some sediment on the surface of nanofibers, which indicates the existence of PDA
coating. Figures 1(d)–(f) shows Ag@PDA@SiO2 nanofibers obtained by glucose reduction of AgNO3 with different concentrations. It can be seen from the figure that the surface of the nanofibers become rough and are decorated with small particles, indicating that silver nanoparticles were successfully coated on the surface of the fibers. It is because that dopamine would be spontaneously polymerized to PDA, which is deposited on the surface of SiO2 nanofibers through chemical bonding. PDA molecule chains are rich of hydroxyl and amino groups, which are combined with Ag⁺ tightly, and by the reaction of glucose, Ag⁺ are reduced to Ag nanoparticles. PDA play a role of ‘bridging ligand’ to combine silver nanoparticles with SiO2 matrix nanofibers [35].

It is seen from figures 1(d)–(f) that the formed Ag nanoparticles exhibit different particles size and load density, after PDA@SiO2 nanofibers are immersed in various concentrations of AgNO3 solution. When AgNO3 concentration is 3 mg ml⁻¹, the formed silver nanoparticles decorated on the surface of the PDA@SiO2 nanofibers are discrete, and the surfaces of fibers are not coated by Ag nanoparticles thoroughly. When the concentration of AgNO3 is increased to 5 mg ml⁻¹, Ag nanoparticles deposited on the surface of the fibers are evenly distributed, densely packed, covering the fibers entirely. When the concentration of AgNO3 is increased furtherly to 10 mg ml⁻¹, it is clearly seen the size of Ag nanoparticles on fibrous become larger than that of the other two samples, and more agglomerated. As shown in figures S1(d)–(f), the mean diameter of Ag@PDA@SiO2 nanofibers increase from 448 nm to 600 nm, which indicates the size enlargement of Ag nanoparticles. Obviously, compared with the diameter of 398 nm of PDA@SiO2 nanofibers (as shown in figure S1(c)), the remarkable increase in composite nanofibers diameter size is owing to the deposition of Ag nanoparticles on the surface of electrospinning nanofibers.

Meanwhile, to investigate the elemental composition of samples, x-ray energy-dispersive spectroscopy (EDS) analysis was performed on Ag@PDA@SiO2 composite nanofibers, as shown in figure S2. It can be clearly seen from the figure that the presence of elemental Si, O, C, N, Ag is detected in the Ag@PDA@SiO2 composite nanofibrous membranes, which is agreed with the chemical composition of the samples. And it is worth noting that the peak intensity and the relative atomic percentage of Ag element gradually increases with the increase of AgNO3 concentration, indicating the load amount of Ag nanoparticles on composite nanofibers is increased. However, combined with figure 1, it is found that the sample obtained with 5 mg ml⁻¹ AgNO3 (i.e. Ag@PDA@SiO2-5) exhibit a relative uniform and compact Ag nanoparticles deposition, which is favorable for the formation of high SERS activities, thus it is chosen for the next performance characterization.

Furthermore, to determine the distribution of silver nanoparticles on the composite nanofibers, the elemental surface distribution analysis of the Ag@PDA@SiO2-5 sample was performed by EDX. Figure 2 shows elemental mapping images of silicon (a), oxygen (b), carbon (c), nitrogen (d), silver (e), and the merged (f) of Ag@PDA@SiO2-5 nanofibers. It can be seen from figure 2 that elements of Si, O, C, N and Ag are observed by energy spectra analysis. As shown in figure 2(a), the elemental mapping of silicon presents a clear profile of a single nanofiber, which is arising from the matrix fiber of SiO2. It’s interesting to found from figure 2(b) that the diameter of oxygen elemental distribution is slightly wider than that of silicon, since a portion of oxygen signals are derived from the phenolic hydroxyl group in PDA. The existence of carbon and nitrogen elements as shown in figures 2(c) and (d) are attributed to the presence of PDA coating layer. As shown in figure 2(e), the

Figure 1. SEM images of nanofibers of SiO2 precursor (a), SiO2(b), PDA@SiO2 (c), Ag@PDA@SiO2-3 (d), Ag@PDA@SiO2-5 (e), Ag@PDA@SiO2-10 (f).
distribution of elemental silver during scanning is identical to the contour of the nanofiber, and the diameter is larger than that of Si and O, which demonstrates that Ag nanoparticles are successfully decorated on the surface of the PDA@SiO2. It is obviously seen from Figure 2(e) that the distribution of silver is rather dense and even, which is beneficial to the Raman enhancement and improve the sensitivity of SERS detection, since the nanoscale gaps between isolated silver particles forms ‘hot spots’ [37]. Compared figure 2(f) with figure 2(a), it’s found that the final as-prepared Ag@PDA@SiO2 composite nanofibers exhibit a multi elemental distribution and a rougher profile, which reflects its actual microscope structure.

In order to observe the distribution of Ag nanoparticles on the surface of nanofibers in a higher magnification scope, the morphologies of the as-prepared electrospinning nanofibers were also characterized by the technique of TEM. Figure 3 shows TEM images of SiO2 (a), PDA@SiO2 (b), Ag@PDA@SiO2-3 (c), Ag@PDA@SiO2-5 (d), Ag@PDA@SiO2-10 (e) nanofibers, and high-resolution electron micrograph of Ag@PDA@SiO2-5 nanofibers (f), the inset is an electron diffraction pattern.

Figure 2. Elemental mapping images of silicon (a), oxygen (b), carbon (c), nitrogen (d), silver (e), and the merged (f) of Ag@PDA@SiO2-5 nanofibers.

Figure 3. TEM images of SiO2 (a), PDA@SiO2 (b), Ag@PDA@SiO2-3 (c), Ag@PDA@SiO2-5 (d), Ag@PDA@SiO2-10 (e) nanofibers, and high-resolution electron micrograph of Ag@PDA@SiO2-5 nanofibers (f), the inset is an electron diffraction pattern.
different contrast is formed on the surface of fiber, as shown in figure 3(b). It indicates the successful coating of PDA on the surface of SiO\(_2\) nanofibers. It can be seen clearly from figures 3(c)–(e) that Ag nanoparticles are decorated on the surface of PDA@SiO\(_2\) nanofibers, after immersion in AgNO\(_3\) solution and reduction by glucose. It’s also found from figures 3(c)–(e) that the mean particles size increase when AgNO\(_3\) concentrations are increased from 3 to 10 mg ml\(^{-1}\). The particles size was measured and its distribution was calculated by a software of ‘Nano measurer’. Figure S3 shows particles size distribution histograms of silver nanoparticles on fibers of Ag@PDA@SiO\(_2\)-3 (a), Ag@PDA@SiO\(_2\)-5 (b), Ag@PDA@SiO\(_2\)-10 (c). It’s worth mentioning that when AgNO\(_3\) concentration is 5 mg ml\(^{-1}\), Ag nanoparticles deposited on PDA@SiO\(_2\) nanofibers exhibit a uniform distribution with an average particle size of 50 nm. Compared figures S1(b) and (e), it’s found that the diameter of nanoparticles increases from 390 nm to 496 nm. In consideration of the particles size of 50 nm, it indicates the coating of Ag nanoparticles is exactly one layer for the sample of Ag@PDA@SiO\(_2\)-5. From the HRTEM image of Ag@PDA@SiO\(_2\)-5 nanofibers, which is shown in figure 3(f), it can be seen that silver nanoparticles decorated on the surface of the fibers have distinct lattice fringes. The lattice spacing between the stripes is 0.23 nm, which is consistent with (111) planes of face-centered cubic (fcc) structured silver crystalline. Furthermore, it can be seen from the inset of electron diffraction pattern that the occurrence of continuous concentric rings, which indicates the polycrystalline nature of silver nanoparticles.

The phase structure of the as-prepared nanofibers was analyzed by XRD. Figure 4(a) shows the diffraction patterns of SiO\(_2\), PDA@SiO\(_2\), and Ag@PDA@SiO\(_2\) nanofibers obtained with different concentrations AgNO\(_3\), respectively. From figure 4(a), it’s seen that the neat SiO\(_2\) electrospinning nanofibers exhibit a broad peak at a diffraction angle of 2\(^{\circ}\), indicating it has an amorphous structure. After the grafting of PDA, no significant change occurs in the pattern of PDA@SiO\(_2\) nanofibers, indicating that surface modification by PDA has no effect on the structure of SiO\(_2\) nanofibers [26]. However, it’s obviously seen from figure 4(a) that new diffraction peaks appear in the patterns of Ag@PDA@SiO\(_2\) nanofibers, after the further surface decorated by silver nanoparticles. The diffraction peaks centered at \(2\theta\) of 38.1\(^{\circ}\), 44.3\(^{\circ}\), 64.3\(^{\circ}\), 77.4\(^{\circ}\), 81.5\(^{\circ}\) are corresponding to the (111), (200), (220), (311), (222) crystal planes in a fcc structural silver (ICPDF, No. 04-0783), respectively [38]. Moreover, the appearance of impurity peaks is not found, indicating that the surface of PDA@SiO\(_2\) nanofibers successfully modified by Ag nanoparticles, which does not contain by-product, such as Ag\(_2\)O. It’s also found from figure 4(a) that the relative intensity of diffraction peak is enhanced gradually with the increase of AgNO\(_3\) concentrations for the samples of Ag@PDA@SiO\(_2\). It is because that when the concentration of AgNO\(_3\) is higher, the particles size and load amount of silver nanoparticles is larger.

Thermal stability is one of the advantages of SiO\(_2\) as matrix electrosprinning nanofibers, thus, TGA characterization was performed on samples. Figure 4(b) shows TGA curves of SiO\(_2\) precursor, SiO\(_2\), PDA@SiO\(_2\) and Ag@PDA@SiO\(_2\)-5 nanofibers. For the sample of SiO\(_2\) precursor nanofibers, its TGA curve can be divided into four stages, as shown in figure 4(b). Firstly, in the raising temperature range of 25 \(^{\circ}\)C~100 \(^{\circ}\)C, the weight loss is about 10.4%, which can be attributed to the volatilization of moisture and residual solvent adsorbed on the surface of the precursor [31, 39]. Secondly, in the temperature range from 100 \(^{\circ}\)C to 390 \(^{\circ}\)C, the sample gradually lose its mass of 10.7%, which is arising from the decomposition of the side chain of PVP and the dehydration reaction of TEOS. Subsequently, this sample exhibit a sharp weight loss in temperature range of 390 \(^{\circ}\)C~500 \(^{\circ}\)C, the whole percentage is about 49.7%, which is due to the decomposition of the PVP backbone and the condensation reaction of TEOS [30, 40]. While, a constant weight loss curve stage is occurring after the temperature reaches to 500 \(^{\circ}\)C, which demonstrates that the employed calcination temperature of 600 \(^{\circ}\)C in this work can guarantee a complete conversion from SiO\(_2\) precursor to SiO\(_2\) nanofibers. Compared TGA curves of neat SiO\(_2\) and PDA@SiO\(_2\) nanofibers; it’s found they exhibit the same tendency. The loss of the initial weight at
the temperature lower than 100 °C can be attributed to the evaporation of water adsorbed by the nanofibers [26, 35]. When the two samples are heated to 800 °C, the total weight loss of neat SiO2 nanofibers is about 15.9%, while it is 26.5% for PDA@SiO2 nanofibers. The extra weight loss is obviously due to decomposition of PDA, which is consistent with the above structure analysis. For the sample of Ag@PDA@SiO2-5 nanofibers, the surface decorated silver nanoparticles cannot decompose, and the relative content of PDA in the composite nanofibers is lower than that of PDA@SiO2 nanofibers. Thus, its total weight loss percentage is about 15.3%. Therefore, compared with polymer matrix electrospinning nanofibers, the as-prepared Ag@PDA@SiO2 nanofibrous membranes exhibit a rather high thermo stability, which is benefit to serving as substrates for SERS detection, because that the laser beam has effect of raising temperature.

The as-prepared electrospinning nanofibrous membranes possess characteristics of free-standing and flexibility. Figure 5 shows the photographs before and after folding for samples of SiO2 (a, d), PDA@SiO2 (b, e), and Ag@PDA@SiO2-5 (c, f), respectively. It can be observed from figure 5 that after PDA functionalization and electroless plating of silver nanoparticles, the color of the SiO2 membranes changes from raw white to grayish brown, and then to black. This result indicate successful grafting of PDA and the following deposition of Ag nanoparticles on the nanofibers surface. It also can be seen from figures 5(d)–(f) that SiO2 nanofibrous membranes have not broken after being folded, even if it was calcinated in high temperature. The samples obtained by further modification of PDA and Ag nanoparticles still maintain excellent mechanical property of SiO2 fibrous membranes [29, 31], which is one of important requirements for a qualified SERS substrate.

3.2. SERS performance for small molecules detection
Before the SERS detection for bacteria, small molecules of 4-MPh and 4-MBA was used as analyte to select the optimal substrate and determine its sensitivity. Figure 6(a) shows SERS spectra acquired by dropping 10⁻¹ mol l⁻¹ of 4-MPh solution onto silicon wafer, neat SiO2 nanofibrous membranes immersed into 10⁻¹ mol l⁻¹ 4-MPh solution, and Ag@PDA@SiO2 nanofibrous membranes immersed into 10⁻³ mol l⁻¹ 4-MPh solution. As is seen from figure 6(a), for the samples of silicon wafer and neat SiO2 membranes, no any Raman signal can be observed, even when the concentration of 4-MPh solution is up to 0.1 mol l⁻¹. It is because that these samples without silver nanoparticles have no SERS activities. By contrast, when Ag@PDA@SiO2 nanofibrous membranes prepared with different concentrations of AgNO₃ were used as SERS substrates, the adsorbed 4-MPh molecules show significant SERS peaks due to the Raman enhancements of attached Ag nanoparticles, although the concentration is only 10⁻³ mol l⁻¹. The SERS bands appear at 390, 639, 824, 1008, 1077, 1168, 1492 and 1598 cm⁻¹, which are consistent with the characteristic Raman absorption peaks of 4-MPh [41, 42]. It’s worth noting that no SERS peaks of SiO2 nanofibrous membranes is observed, unlike some substrates having SERS bands of themselves, e.g. TiO₂ [27]. Thus, it can be proposed that no interference peak is another advantage of the as-prepared Ag@PDA@SiO2 nanofibrous membranes using as SERS substrate. It also can be seen from figure 6(a) that the SERS bands of 4-MPh collected by Ag@PDA@SiO2-5 shows higher intensity than that of the other composite nanofibrous membranes, which implies that Ag@PDA@SiO2-5 possess the best
SERS activities among the three samples. The reason is attributed that the uniform and compact distribution of silver nanoparticles is favorable for the formation of SERS ‘hot spots’, as revealed by the above morphology and structure analysis. In order to get known its sensitivity, a series of 4-MPh solution with different concentration was formulated and tested. Figure 6(b) shows SERS spectra of 4-MPh at concentrations of $10^{-3} \sim 10^{-11}$ mol l$^{-1}$ collected by using Ag@PDA@SiO$_2$-5 membranes as substrates. As shown in figure 6(b), the SERS peak intensity decreases along with the dilution of 4-MPh concentrations, taking the band centered at 1077 cm$^{-1}$ as an example. However, this characteristic peak of 4-MPh can still be detected, even though the concentration is reduced to $10^{-11}$ mol l$^{-1}$. In other words, the detection limitation for 4-MPh using Ag@PDA@SiO$_2$-5 membranes as SERS substrates is about 1 ppt.

To verify the universality of this SERS substrate, another common small probe molecule of 4-MBA was also detected. Figure 6(c) shows SERS spectra of 4-MBA acquired by using silicon wafer, neat SiO$_2$ and Ag@PDA@SiO$_2$ nanofibrous membranes as substrates, respectively. As can be seen from figure 6(c), for the substrates of Ag@PDA@SiO$_2$ nanofibrous membranes, the SERS spectra show significant Raman characteristic peaks of 4-MBA at 524, 1080, 1186 and 1589 cm$^{-1}$, respectively [37, 43]. Furthermore, it’s also found that Ag@PDA@SiO$_2$-5 exhibit the highest SERS activity among the three samples, similar as the detection for 4-MPh. The detection limitation for 4-MBA of this substrate was also tested, as shown in figure 6(d), and an ultrahigh sensitivity of $10^{-11}$ mol l$^{-1}$ can be verified. Nevertheless, by comparison of figures 6(d) and (b), it’s reasonable to affirm that the as-prepared composite nanofibers have superior SERS effect on 4-MBA than 4-MPh. Since for the same concentration of small molecule probe solution, their SERS peak intensities are different (the relative intensity scale bar is 10000 and 20000, respectively). Thus, it can be concluded that Ag@PDA@SiO$_2$ nanofibrous membranes as SERS substrates for small molecule probe detection have outstanding detection sensitivity and versatility, and exhibit better SERS activity than our previous [27] and other’s similar work [44].

### 3.3. SERS performance for bacteria detection

SERS detection of two small molecule probes verified that the as-prepared SERS substrate exhibited ultrahigh detection sensitivity. Thus, it was conducted to identify the bacteria strains through direct SERS detection without the binding of bacteria cells with Ag nanoparticles through aptamer. Figure 7 shows SERS spectra of E. coli (a) and S. aureus (b) by using SiO$_2$ and Ag@PDA@SiO$_2$ nanofibrous membranes as substrates. As shown in figure 7(a), no any Raman peaks appears for neat SiO$_2$ nanofibrous membranes substrate. In contrast, for the
three Ag@PDA@SiO2 nanofibrous membranes substrates, clear and analogous SERS peaks are detected, due to the Raman enhancement effort from Ag nanoparticles decorated on fibers surface. The prominent SERS peaks of E. coli appear at 654, 726, 1319 cm$^{-1}$, are corresponding to the absorption vibration of tyrosine [45], adenine [3] and guanine [46], respectively. It also can be seen from figure 7(a) that the sample of Ag@PDA@SiO2-5 substrate exhibit the highest signals intensity, indicating it possess the maximal Raman enhancement effect. Figure 7(b) shows that the similar detection results on S. aureus as those of E. coli. The main SERS characteristic peaks of S. aureus appear at 731, 1330 1445 and 1575 cm$^{-1}$, which are corresponding to the absorption vibration of adenine [15], guanine [11], saturated lipid and amide II of proteins [27]. Similarly, the SERS peak intensity obtained from Ag@PDA@SiO2-5 substrate is much higher than that of the other two samples. Furthermore, by compassion of peak intensity of these two bacteria strains, it’s found that the peak intensity of S. aureus is much higher than that of E. coli, indicating that the as-prepared Ag@PDA@SiO2 nanofibers has higher SERS sensitivity for detection of S. aureus. The above detection results demonstrate that Ag@PDA@SiO2 nanofibrous membranes using as SERS substrate can identify different germs quickly and directly without aptamer or probe labeling.

Besides high sensitively, the repeatability is another important requirement for a qualified SERS substrate, which is dependent on the structural homogeneity of materials. Therefore, a total of 20 points was randomly selected on the substrate of Ag@PDA@SiO2-5 nanofibrous membranes to evaluate its uniformity and reproducibility, and the collected SERS spectra are shown in figures 8(a), (c), for E. coli and S. aureus, respectively. It can be seen from figures 8(a), (c) that either the peak positions or the peak intensities are rather in accordance for the both bacterial strains. Furthermore, the relative standard deviation (RSD) of peak’s intensity at 658 cm$^{-1}$ and 733 cm$^{-1}$ were calculated for E. coli and S. aureus, as shown in figures 8(b), (d), respectively. The results are 7.7% and 6.8% for the two analytes, which are superior than the value of 25% for E. coli detection by other researchers’ composite electrospinning nanofibrous membranes [47]. Thus, it’s suggested that the as-fabricated SERS substrate exhibit an excellent reproducibility, which is attributed to the uniform distribution of Ag nanoparticles on electrosprinning nanofibers, and the crisscrossed arraying of fibers.

3.4. Antibacterial property of Ag@PDA@SiO2 nanofibrous membranes

Except for the excellent SERS activities, the as-prepared Ag@PDA@SiO2 nanofibrous membranes are certainly possess antibacterial properties, since it’s one of the characteristics of Ag nanoparticles. Herein, its antimicrobe activities were evaluated through methods of inhibition zone and turbidity method. Figures 9(a), (b) shows photographs of inhibition zones for SiO2, PDA@SiO2, Ag@PDA@SiO2 nanofibrous membranes against E. coli and S. aureus, respectively. It can be seen from figures 9(a), (b) that no inhibition zone appears around samples of SiO2 and PDA@SiO2, indicating that they have no antibacterial effect on bacteria. However, when silver nanoparticles are decorated on the surface of nanofibers, for the sample of Ag@PDA@SiO2 nanofibrous membranes, clear inhibition zones are found against the both bacteria strains. Meanwhile, it’s obviously seen from figures 9(a), (b) that inhibition rings around Ag@PDA@SiO2-5 are bigger than that of the other two samples. The results demonstrate that Ag@PDA@SiO2 nanofibrous membranes have significant antibacterial properties, especially for sample of Ag@PDA@SiO2-5. In order to compare the concrete inhibition zones data of the three Ag@PDA@SiO2 samples, the difference values between outer ring and inner ring of the inhibition zones after interaction of Ag@PDA@SiO2 nanofibrous membranes with bacteria are measured, calculated and shown in figure 9(c). It’s seen from figure 9(c) that the D-values for Ag@PDA@SiO2-5 against E. coli and S. aureus are 5.0 and 4.3, respectively. By comparison, these values are 3.2, 2.6 for Ag@PDA@SiO2-3, and 2.1, 2.3

Figure 7. SERS spectra of E. coli (a) and S. aureus (b) by using SiO2 and Ag@PDA@SiO2 nanofibrous membranes as substrates.
for Ag@PDA@SiO₂-10. The results verify further that Ag@PDA@SiO₂-5 possess the best antibacterial activities, the reason can be attributed to its appropriate particles size and uniform distribution.

Besides inhibition zones, the method of turbidity was also employed to evaluate further the antibacterial activities. Figure 9(d) shows the absorbances values of bacteria suspension at the peak of 600 nm for blank bacteria, neat SiO₂, PDA@SiO₂, and Ag@PDA@SiO₂ nanofibrous membranes against E. coli and S. aureus. It can be seen from figure 9(d) that the absorbances of bacteria suspension after the action by SiO₂ and PDA@SiO₂ are approximate with that of the blank bacteria, indicating the both samples have no obvious antibacterial properties. On the contrary, all the suspensions containing Ag@PDA@SiO₂ nanofibrous membranes exhibit significant lower absorbance, especially for the sample of Ag@PDA@SiO₂-5. The decreasing of turbidity means that the number of survival bacteria are reduced, due to the antibiosis effect of Ag nanoparticles from composite nanofibers. This result is consistent with the conclusion obtained through the test of inhibition zone method.

3.5. Antibacterial mechanism of Ag@PDA@SiO₂ nanofibrous membranes

To reveal the probable antibacterial mechanism, the morphology changes in bacteria cells were observed through the technique of SEM. Figure 10 shows SEM images of the normal bacteria (a, b) and the treated bacteria by Ag@PDA@SiO₂-5 nanofibrous membranes (c, d) for E. coli and S. aureus, the inserted arrows indicate the sites where severe damages on cells occurring. It can be seen from figure 10(a) that the normal E. coli cells exhibit a uniform short rod morphology with smooth cell surfaces. By contrast, the morphology of E. coli cells has changed significantly after the action of Ag@PDA@SiO₂-5 nanofibers, as shown in figure 10(c). The bacteria cells are not only shrunk, but also broken, accompanied with the leakage of internal matters. Similarly, as shown in figure 10(b), the untreated S. aureus cells show a smooth and complete spherical shape, while the surface of the cells treated with Ag@PDA@SiO₂-5 nanofibers (figure 10(d)) exhibit sunken, broken and other damaged phenomena. In addition, it can be clearly seen from figures 10(c), (d) that the detached silver nanoparticles and the cleavage Ag@PDA@SiO₂ nanofibers interact with the bacteria cells, thereby causing apoptosis of the bacterial cells. The results demonstrate the direct contact antibacterial mechanism of silver nanoparticles. This hypothesis mechanism proposes that silver nanoparticles can be adsorbed on the surface of bacterial cell membrane by electrostatic interaction, and bind to polysaccharides and proteins on the outer membrane of bacteria, so that the normal physiological functions of the cells are destroyed, leading

Figure 8. SERS spectra of E. coli (a) and S. aureus (c) collected from 20 randomly selected positions on Ag@PDA@SiO₂-5 substrate surfaces, and histograms of intensity distribution for characteristic Raman peaks at 658 cm⁻¹ (b) from E. coli and at 733 cm⁻¹ (d) from S. aureus, respectively.
to apoptosis [16, 48]. In addition, the action of nanofibers and bacteria may also be arising from the release mechanism of Ag$^+$. Silver nanoparticles can release Ag$^+$ due to their interaction with O$_2$ and H$_2$O in ambient surroundings. Ag$^+$ can enter the cells and combine with the electron donating group, thereby destroying the normal metabolism of the cells [49, 50].

4. Conclusion

In summary, a facile approach has been presented to fabricate Ag@PDA@SiO$_2$ nanofibrous membranes by electrospinning and surface chemical modification, for label-free SERS detection on bacteria. The morphology and structure of the as-prepared electrospinning nanofibrous membranes were analyzed by techniques of SEM, TEM, EDX, XRD and TGA. The results show that for the sample of Ag@PDA@SiO$_2$-5, Ag nanoparticles with an average diameter of 50 nm, are distributed on nanofibers even and densely, which promote the formation of ‘hot spots’ for SERS detection. Furthermore, it’s demonstrated that the as-prepared free-standing Ag@PDA@SiO$_2$ nanofibrous membranes possess flexibility and high thermostability, which are benefit for its application as SERS substrate. The SERS detection for small molecules probes of 4-MPh and 4-MBA by employing Ag@PDA@SiO$_2$ nanofibrous membranes as substrates exhibit an ultrahigh sensitivity of $10^{-11}$ mol l$^{-1}$ (i.e. a detection limitation of about 1 ppt). More importantly, it can be directly subjected to the SERS for bacteria identification, such as E. coli and S. aureus, without pretreatment. This bacteria detection not only is label-free, but also exhibits good reproducibility. Therefore, Ag@PDA@SiO$_2$ nanofibrous membranes as SERS substrates have certain practical significance in the detection of trace chemicals and bioanalytical sensing. In addition, the as-prepared Ag@PDA@SiO$_2$ nanofibrous membranes exhibit excellent antibacterial activity against both Gram-negative bacteria of E. coli and Gram-positive bacteria of S. aureus.
Acknowledgments

The authors thanks for the financial support from National Natural Science Foundation of China (Grant No. U1604126), the Postgraduate Education Innovation and Quality Promotion Program of Henan University (Grant Nos. SYL19060166 and SYL19060101), the Interdisciplinary Research for First-class Discipline Construction Project of Henan University (Grant No. 2019YLXKJC04), and 2019 Medical Interdisciplinary Cultivation Project of Henan University (Grant No. CJ1205A0240013).

ORCID iDs

Lei Sun  https://orcid.org/0000-0002-8112-2055

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