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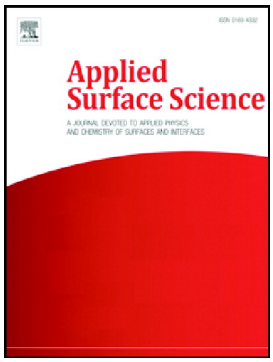

Hydraulically pressed silver nanowire-cotton fibers as an active platform for filtering and surface-enhanced Raman scattering detection of bacteria from fluid

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Hydraulically pressed silver nanowire-cotton fibers as an active platform for filtering and surface-enhanced Raman scattering detection of bacteria from fluid

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Abstract

Silver and gold nanoparticles-decorated cotton fiber substrates constitute an important group of the simple, inexpensive and versatile platforms for a SERS-based detection of biomolecules. However, the fibrous cotton embedded with metal nanoparticles is yet to be explored as a filter-like substrate for isolation and detection of pathogens from fluid. In this study, we present a straightforward approach based on hydraulic pressing to make a silver nanowire-decorated cotton fibers substrate a realistic platform for effective filtering and detection of bacteria from

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urine. Silver nanowires were anchored on cotton fibers using an aminopropyltrimethoxysilane as a linker. The obtained silver nanowire-cotton fiber material was compressed with a hydraulic press to substantially reduce the free spaces between the individual fibers. As a proof-of-concept, the prepared substrate was employed to effectively filter *Escherichia coli* bacteria from phosphate-buffered saline solution and urine. The silver nanowire-cotton SERS substrate thus serves as a low-cost and active platform for an effective detection of bacteria from fluids.

Keywords; surface-enhanced Raman scattering, cotton, silver nanowire, *Escherichia coli*, bacteria.

1. Introduction

Pathogenic bacteria are responsible for many fatal and serious diseases [1]. Due to the negative effect of bacterial infections, attention over the years has been focused on their accurate detection in food, water, and different body fluids [2]. The accurate assay of foodborne and waterborne pathogens is imperative in the areas of medical diagnosis and environmental monitoring. Lately, surface-enhanced Raman spectroscopy (SERS) has found a wide use in the field of sensing, due to its ability of providing fingerprint information about molecular species [3]. Thus, SERS can function as a label-free technique to identify toxins [3], drugs [4], DNA [5], cancer cells [6], and bacteria [7].

The SERS phenomenon, which is based on plasmonic metal nanoparticles, is generally attributed to electromagnetic and chemical enhancement mechanisms [8–10]. The SERS effect is highly dependent on the type and nature of the metal nanoparticle. Therefore, efforts have been focused on the fabrication of highly active and sensitive SERS substrates having nanoparticles in various sizes, shapes and compositions [3,11,12].

Active SERS substrates for the detection and identification of bacteria have been achieved via different approaches. One approach involves a direct synthesis of metal nanoparticles of gold or silver on the surface of bacteria or inside bacteria prior to the SERS measurement [7,13–15]. Another approach consists of mixing a colloidal solution of metal nanoparticles with bacteria and the mixture is drop-dried on a flat surface before the SERS spectral acquisition [16–18]. A third approach involves placing bacteria on a prepared SERS substrate [19–22]. The substrate in this case can be nanoparticles on a porous or non-porous support material. Porous SERS-active substrates are of a great interest in bacterial analysis because such platforms could function as filters, as well. Porous SERS-active substrates thus provide the possibility to isolate, concentrate and immobilize bacteria from a matrix. Bacteria such as *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Salmonella typhimurium,* and *Escherichia coli* have been isolated and detected using porous SERS-active substrates such as gold nanoparticles in a mesoporous silica [23], silver nanoparticles on a porous anodic aluminum oxide (AAO) [24], nanoparticle-decorated polymer mats prepared through electrospinning [25] or forcespinning [26], and a porous polymer monolith with embedded gold nanoparticles [27].

Cotton fibers as a support material for a gold or silver nanoparticle deposition have attracted a considerable interest in recent years [28,29]. One reason is the low-cost of cotton fibers, and another is their readily accessibility. Cotton or cotton woven fabric decorated with metal nanoparticles of gold or silver have been used as flexible SERS-active materials [30–33] for trace analysis of explosives and insecticides. In this study, we explore further fabrication of cotton fibers decorated with nanoparticles into a filter-like material for trapping and detection of bacteria from fluids (Figs. 1 and 2). Nanowires of silver, as a highly sensitive SERS material, were anchored on cotton fibers using 3-aminopropyltrimethoxysilane as a linker. The resulting

composite material was carefully compressed using a hydraulic press into a robust and porous SERS substrate for isolation and detection of bacteria. The use of the ordinary cotton material thus makes the new substrate cost-effective compared to the conventional porous SERS-active substrate used for bacteria detection from fluids.

2. Experimental

2.1. Chemicals

Silver nitrate ($AgNO_3$, Merck), sodium citrate tribasic dihydrate (Aldrich, ≥ 99%) were used in the synthesis of silver nanowires. The surface of cotton fibers (100 % cotton, IISi, Tokmanni Oy) was modified with 3-aminopropyltrimethoxysilane (APTES, Aldrich ≥ 99 %) in ethanol (Altia, 99.5 %). *Escherichia coli* XL1-Blue (OD = 1.68) was used for the study. Luria broth (Merck, 1% peptone, 1% NaCl, 0.5% yeast extract) was used as microbial growth medium for *E. coli* bacteria. Phosphate-buffered saline (PBS 138 mM of NaCl, 2.7 mM of KCl, and 10 mM of phosphate pH = 7.2) was used to wash the *E. coli* bacteria sample. Glutaraldehyde (Aldrich) and hexamethyldisilizane (HMDS, Aldrich ≥ 99%) where used in fixing and drying *E. coli* bacteria prior to the SERS measurement. Hematin (Aldrich), 4-aminothiophenol (4-ATP, Aldrich 97%), and adenine (Aldrich ≥ 99%) were used as probe molecules to investigate the sensitivity of the SERS substrate. Milli-Q water (18.4 MΩ cm^{-1}) was used in all reactions in aqueous medium.

2.2. Synthesis of silver nanowires

A one-pot procedure reported by Anker *et al.* [34] was employed in the synthesis of the silver nanowires without any modifications. In a typical reaction, 100 µl of 0.1 M sodium citrate was added to 100 µl of 0.1 M $AgNO_3$ solution. The resulting mixture was diluted to a volume of 100 ml, and carefully covered with aluminum foil. The silver nanowire precursor was then placed in

a pre-heated oven (130 °C) for 3h. After the 3h heating, the silver nanowire suspension was removed from the oven and allowed to cool under ambient conditions. Finally, the nanowire suspension was centrifuged to remove all unreacted reagents and dispersed in 2 ml of water.

2.3. Preparation of silver nanowires decorated cotton fibers

The cotton fibers were modified with 3-aminopropyltrimethoxysilane (APTES) according to the procedure reported by Qu *et al*. [31]. In this process, 20 mg of cotton fibers were incubated in an ethanolic solution of 2% APTES and ultra-sonicated in an ultrasonic bath for 30 min. After sonication, cotton fibers are completely dispersed in the ethanolic solution and no visible wad is present. The APTES modified cotton fibers were washed 3 times with ethanol and dried at 120 °C for 30 min. The modified cotton fibers were incubated in the 2 ml silver nanowire solution for 30 min. The silver nanowire decorated cotton fibers were finally dried at 40 °C for 1 h.

2.4. Preparation of silver nanowire-cotton SERS substrate

The silver nanowire decorated cotton fibers were pressed into a flexible pellet using a hydraulic press (Fig. 1). A pressure of 5 tons was applied in the preparation of the pellet.

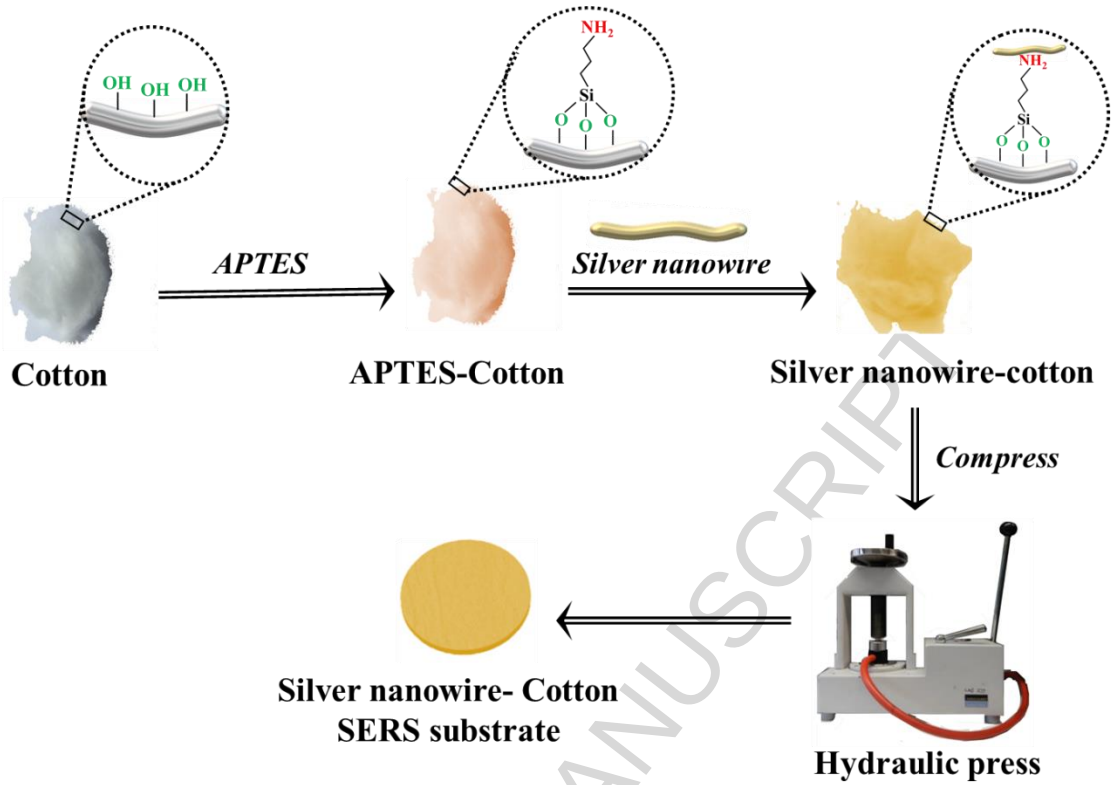


Fig. 1. A schematic illustration for the fabrication process of the silver nanowire-decorated cotton SERS substrate. The thickness and diameter of the compressed silver nanowire-decorated cotton substrate are about 0.034 cm and 1.3 cm, respectively.

2.5 Culturing of E. coli bacteria

E. coli XL1-blue bacteria were streaked out from a glycerol stock solution onto a Luria broth agar plate containing 10 µg/ml tetracycline and cultured at 37 °C for about 18 h. A colony of the *E. coli* bacteria was then transferred into 5 ml Luria broth with 10 µg/ml tetracycline and kept in an incubator (37 °C, 150 rpm) to grow overnight. The concentration of the bacteria was estimated using a spectrophotometer to be about 1.04×10^9 cells/ml.

2.6. SERS-based detection of E. coli using silver nanowire-cotton SERS substrate

The *E. coli* XL1-blue bacteria were pelleted from the Luria broth culture medium and washed 3 times with phosphate-buffered saline (PBS). Finally, the *E. coli* bacteria were suspended in 2 ml of PBS or urine solution. About 1 ml of the PBS or urine *E. coli* bacteria suspension was poured on the silver nanowire-cotton following the procedure presented in Fig. 2. The silver nanowire-cotton with bacteria sample was thoroughly washed with Milli-Q water. After a 5 min incubation of the composite under ambient conditions, the SERS measurement can be done outright, or additional silver nanowires can be added to the bacteria entrapped area for an enhanced SERS signal.

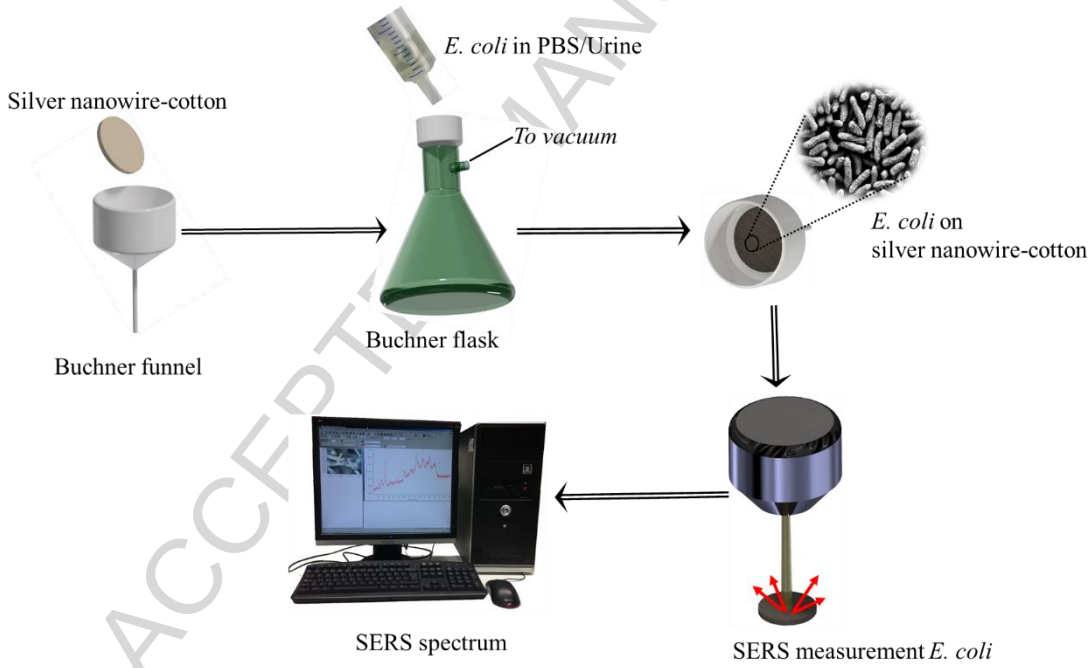


Fig. 2. A schematic illustration of the trapping of *E. coli* bacteria from a PBS solution or urine on a silver nanowire-cotton substrate for a SERS measurement.

2.7. Estimation of the analytical enhancement factor (AEF) of the silver nanowire-cotton fibers substrate

The analytical enhancement factor (*AEF*) of the silver nanowire-cotton fibers platform towards 4-aminothiophenol was estimated with equation 1 [35]

$$AEF = \frac{I_{SERS}}{I_{Raman}} \times \frac{C_{Raman}}{C_{SERS}} \quad (1)$$

where I_{SERS} is the intensity of 4-aminothiophenol band at 1070 cm^{-1} recorded on the silver nanowire-cotton fibers, C_{SERS} is the concentration of the probe molecule giving rise to I_{SERS}, I_{Raman} is the intensity of the probe molecule collected on a clean glass slide, and C_{Raman} is the concentration of the probe molecule giving rise to I_{Raman}. The *AEF* of the silver nanowire-cotton fibers was about 1×10^6 in different positions of the substrate.

2.8. SERS signals reproducibility of the silver nanowire-cotton fibers substrate

The signal reproducibility of the silver nanowire-cotton SERS substrate was determined with adenine (100 µM). Ten different SERS spectra of adenine were recorded on the silver nanowire-cotton substrate and the confidence level of the 732 cm^{-1} signal intensity from the measurements was estimated. The 95% confidence level from 10 different measurements was found to be 7.5% of the mean value.

2.9. Characterization

The morphology of silver nanowires and the silver nanowire-cotton fibers platform were observed with a Hitachi S-4800 FE-SEM (field emission scanning electron microscope). The diameter and length of the silver nanowires and the distance between cotton fibers were analyzed with a PCI image processing tool fitted to the Hitachi S-400 FE-SEM. The *E. coli* on silver

nanowire-cotton substrate was observed with a Zeiss Sigma HD|VP SEM (Carl Zeiss NTS, Cambridge, UK) after a dehydration process, which is shortly described as follows: the substrate samples containing bacteria were first fixed with 2.5% glutaraldehyde in phosphate-buffered saline (PBS) for 1 hour. After the fixation, the substrates were twice washed in PBS (2 times, 10 min each) and dehydrated in the ascending ethanol series (50, 60, 70, 80, 90, 94 and 99.5%, 5 min each). Hexamethyldisilazane (HMDS) was used in the final phase of dehydration to dry the samples (2 times, 10 min each). The samples were finally sputtered with gold prior to the SEM imaging. The plasmonic absorption of the silver nanowires was measured with a Perkin Elmer Lambda 900 UV/Vis/NIR spectrophotometer. A Renishaw inVia Raman spectrometer using a wire 3.4™ software, 514 nm excitation wavelength and 15 µW laser power, were used to record all SERS spectra.

3. Results and discussion

3.1. Design and fabrication of a silver nanowire-cotton fibers SERS substrate

Citrate-capped silver nanowires with a diameter of 54 ± 0.7 nm and a length ranging from 0.3 to 6 µm were prepared and used as SERS-active metal (Fig. 3(a)). The diameter and length of the silver nanowires were estimated from the SEM image of 50 nanowires. The maximum absorption of the prepared silver nanowires was observed around 400 nm in the visible region of the electromagnetic spectrum (Fig. 3(b)). The prepared silver nanowires were anchored onto the surface of cotton fibers using 3-aminopropyltrimethoxysilane (APTES) as a linker molecule [31].

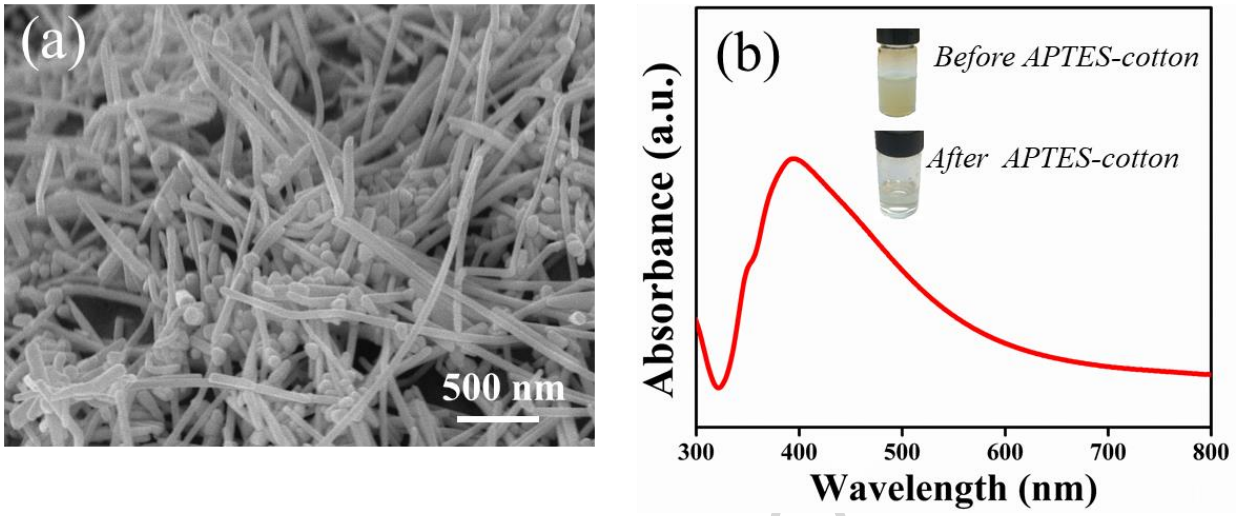


Fig. 3. (a) FE-SEM image of silver nanowires with a diameter of 54 ± 0.7 nm, (b) UV-vis spectrum of silver nanowire colloid. The inset shows colloidal solutions of as-prepared silver nanowires before and after APTES-functionalized cotton fibers incubation.

Prior to an anchorage of silver nanowires, the surface of the cotton fiber was functionalized with APTES. The functionalization was achieved via a coupling reaction of surface hydroxy (−OH) groups of the cotton fibers and silanols from the hydrolyzed APTES (Fig. 2) [36]. After the functionalization, the free amino groups ($-NH_2$) of the APTES form coordination bonds to the silver nanowires via the nitrogen atoms. The immobilization of the silver nanowires onto the APTES-modified cotton fibers results in a de-coloration of the silver nanowire suspension (from grey to colorless) and a coloration of the cotton (from white to dark brown). Silver nanowire-decorated cotton fibers were carefully dried and pressed into a cylindrical pellet using a hydraulic press (Fig. 1). The hydraulic pressing allows a compression of the silver nanowire-cotton fibers into a robust material and assists to decrease substantially the spaces between the

individual cotton fibers, thus making the substrate a realistic material for filtering. As shown in Figs. 4(a) and (b), the spaces of as high as 50 μm between cotton fibers in the pristine substrate can be decreased considerably to as low as 300 nm upon compression, while the silver nanowires still maintain their cylindrical morphology (Fig 4 (c)). The thickness of the compressed silver nanowire-cotton substrate was measured with a Vernier caliper and found to be 0.034 cm. The mass density of the cylindrical substrate having a diameter of about 1.30 cm and a mass of about 0.0209 g was found to be 0.46 g/cm^3.

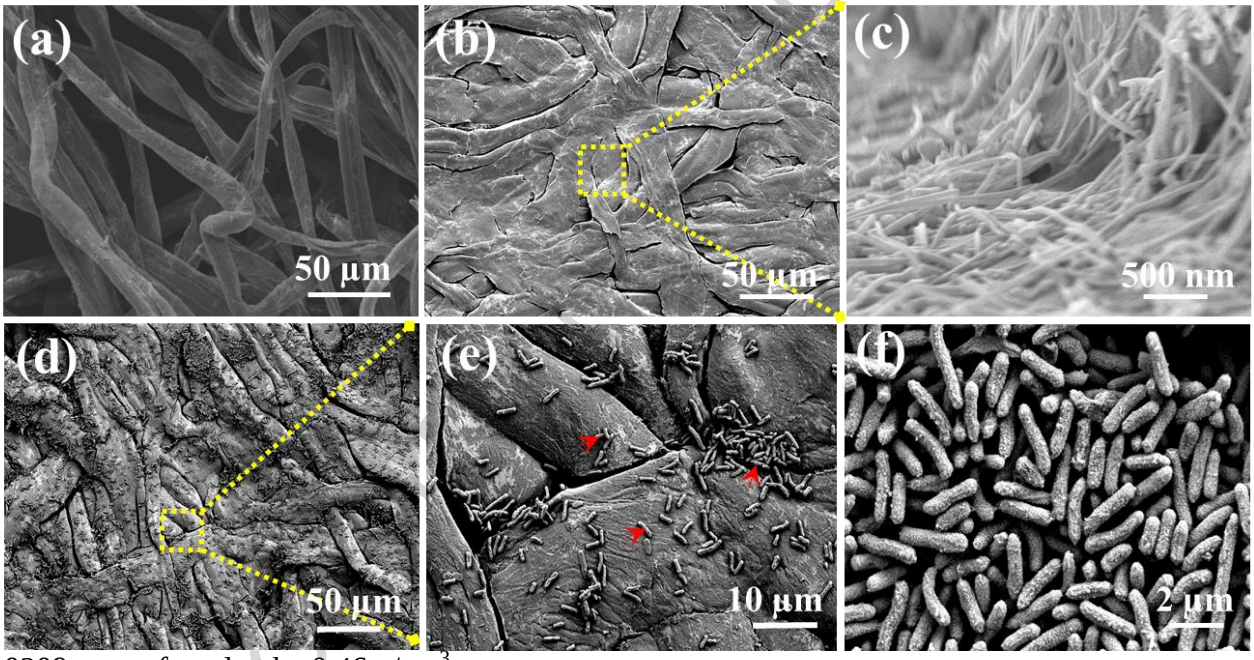


Fig. 4. FE-SEM images of (a) pristine silver nanowire-cotton, (b) and (c) silver nanowire-cotton fibers after compression. HD|VP SEM images of (d) – (f) *E. coli* bacteria trapped on silver nanowire-cotton fibers. Red arrows highlight selected *E. coli* bacteria in (e).

3.2. SERS properties of silver nanowires-cotton fibers

In order to investigate the SERS properties of the silver nanowires-cotton fiber substrate, SERS spectra of two probe molecules were measured and recorded. Fig. 5 shows the SERS profiles of 4-aminothiophenol and adenine recorded on the prepared substrates. In Fig. 5(a), the characteristic 4-aminothiophenol bands are observed around 1070 cm^{-1} and 1592 cm^{-1} and can be assigned to the C-S and C-C stretching, respectively [37]. The prominent characteristic bands for adenine [38] were observed at 732 and 1331 cm^{-1} (Fig. 5 (b)).

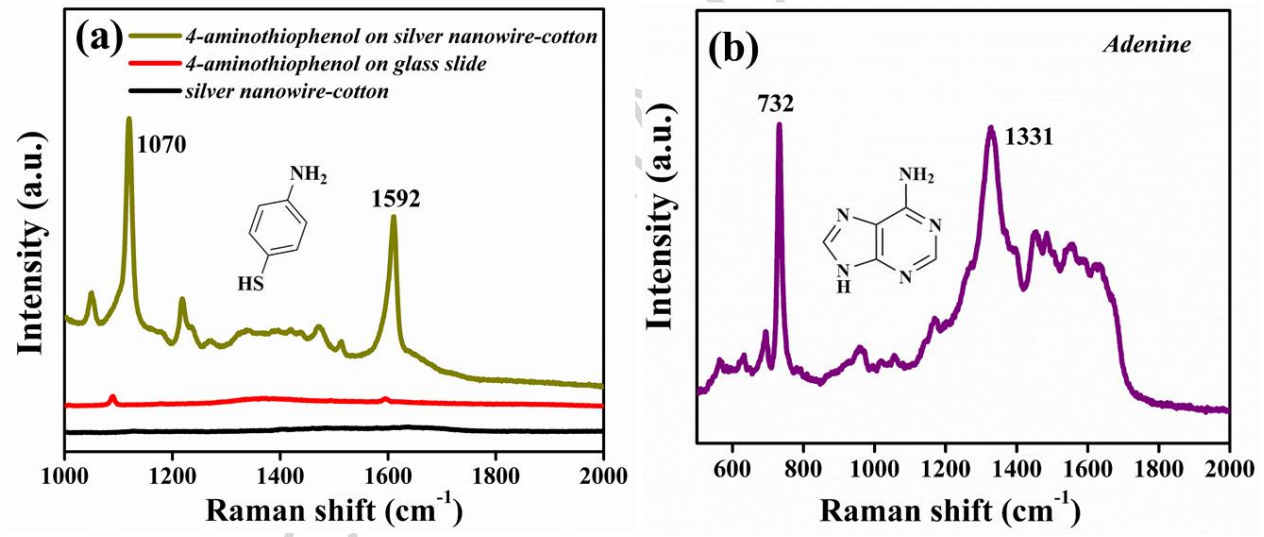
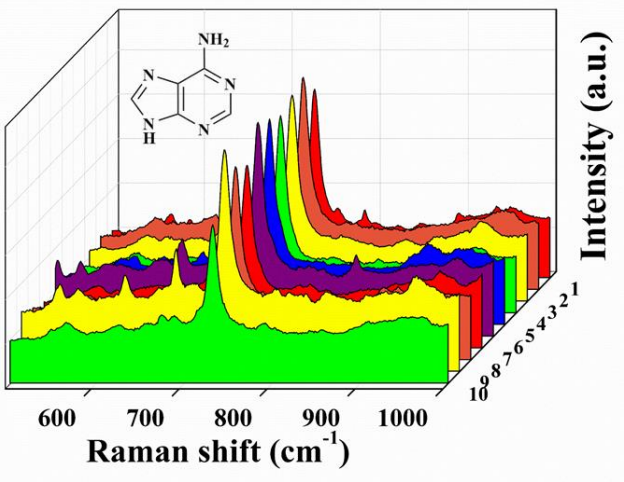


Fig. 5. (a) A SERS measurement of 4-aminothiophenol (1 µM) measured on silver nanowire-cotton and 4-aminothiophenol (0.01M) measured on a glass slide. (b) A SERS measurement of adenine (100 µM) measured on silver nanowire-cotton substrate.

The signal reproducibility of the silver nanowire-cotton substrate of ±7.5 % indicates that the silver nanowire-cotton substrate has a good signal reproducibility (Fig. 6). The analytical

enhancement factor [35] and the detection limit (the lowest concentration the substrate can detect) were examined using a 4-aminothiophenol probe molecule and were found to be about



1×10^{6} and 1×10^{-9} M, respectively.

Fig. 6. SERS spectra of adenine (100 μM) measured on silver nanowire-cotton substrate from 10 random spots. The band at 732 cm^{-1} was used for determination of the signal reproducibility of the substrate.

3.3. SERS-based detection of E. coli bacteria from fluids

Fig. 2 illustrates the procedure employed in a filtering and SERS-based detection of *E. coli* bacteria from fluid using the hydraulically pressed silver nanowire-cotton substrate. The bacteria in the culture medium (Luria broth) were first isolated and purified with a phosphate-buffered saline (PBS) solution to allow the removal of any species in the growth medium that are capable of interfering with the SERS measurement. As a proof-of-concept, *E. coli* bacteria in PBS or urine were first filtered out by the silver nanowire-cotton fiber substrate, based on the procedure shown in Fig. 2. The hydraulically pressed substrate filters out *E. coli* bacteria from fluid onto its

surface and allows a passage of fluid through its pores. The trapped *E. coli* are then detected by SERS using the silver nanowires on the cotton fibers.

The SERS spectrum of the *E. coli* XL1 blue (Fig. 7 (a)) recorded on the silver nanowire-cotton SERS substrate is consistent with the one reported by Haisch *et al*. [39] for the same bacteria, in the case where the silver nanoparticles were synthesized directly on the *E. coli*. Since surface-enhanced Raman scattering is a very short-range phenomenon, only the surface protein of the bacteria, probably in the cell wall, can be detected. *E. coli* XL1-blue is a gram-negative bacterium, and the prominent bands observed around 655 and 725 cm^{-1} can be assigned to the bands originating from guanine and adenine, respectively [39]. Bands around 961 cm^{-1}, 1244 cm^{-1} and 1321 cm^{-1} can be tentatively assigned to aromatic ring breathing [39], amide III [40] and adenine [39], respectively. The band at 1463 cm^{-1} is probably due to saturated lipids [41] and those at 1587 cm^{-1} and 1620 cm^{-1} can be attributed tentatively to signals originating from DNA [41].

The bacterial filtering and trapping efficiency of the silver nanowire-cotton fiber platform was demonstrated by comparing the SERS results to that of silver nanowires on a glass plate. As shown in Fig. 7 (a), after a thorough rinse of *E. coli* bacteria placed on silver nanowires supported on a glass plate with water, the characteristic SERS signals decreased significantly, while prominent signals of *E. coli* were detected on the silver nanowire-cotton substrate after a similar rinsing. This indicates that the fibrous silver nanowire-cotton fibers substrate is efficient in trapping and detection of bacteria from fluid. The enhanced adsorption of the *E. coli* bacteria on the silver nanowire-cotton may be due to the high hydrophilicity of the substrate. The unreacted −OH groups of the cotton can actively interact with the bacteria. Moreover, the interaction may also result from unbound amino groups of the APTES on the cotton. These

possible interactions may have aided the strong adsorption of the *E. coli* bacteria on the silver nanowire-cotton SERS platform.

A silver nanowire-cotton fiber substrate was used under realistic conditions to detect *E. coli* bacteria from a 100 % urine sample. A SERS spectrum of the urine sample on the silver nanowire-cotton substrate was first recorded, and the bands around 676 and 1001 cm^{-1} in Fig. 7 (b), most probably originate from creatinine and urea, respectively [42]. After a thorough rinsing of the silver nanowire-cotton fiber substrate containing the urine sample with water, the urea crystals were substantially washed off, leading to a decrease in the band around 1001 cm^{-1}. Despite these two bands, *E. coli* bacteria can still be clearly detected and identified as shown in Fig. 7(b).

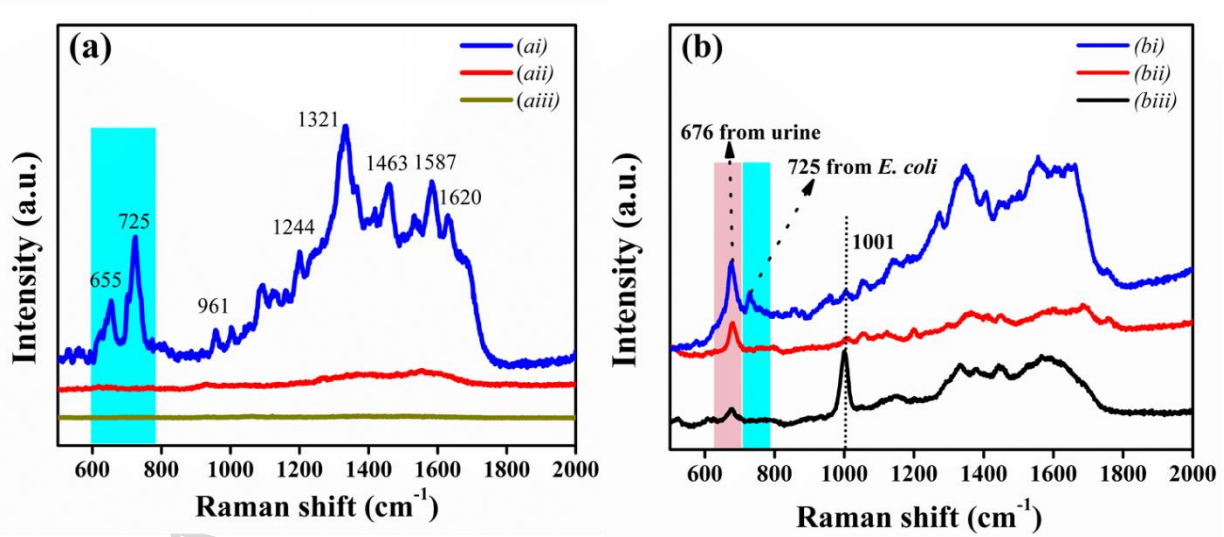


Fig. 7. (a) SERS spectra of *(ai) E. coli* bacteria trapped from PBS with a silver nanowire-cotton substrate and measured after rinsing, *(aii) E. coli* bacteria dropped on a glass slide and measured after rinsing, *(aiii)* silver nanowire-cotton without *E. coli*. (b) SERS spectra of *(bi) E. coli* bacteria trapped from 100 % urine with a silver nanowire-cotton substrate and measured after

rinsing with water, *(bii)* a urine sample on silver nanowire-cotton measured after rinsing, *(biii)* the urine sample on silver nanowire-cotton measured before rinsing.

4. Conclusion

In this study, a filter-like silver nanowire-cotton fiber membrane was prepared. Cotton fibers were first decorated with silver nanowires, and the obtained substrate was compressed with a hydraulic press into a porous membrane. The composite material served as an active SERS platform with an enhancement factor and a detection limit of 1×10^{6} and 1×10^{-9} M respectively, toward 4-aminothiophenol. In addition, SERS signals recorded on the substrate were reproducible. The confidence level of 10 random spectra of adenine measured on the substrate was ± 7.5%. It was also demonstrated that the silver nanowire-cotton SERS substrate can be used as a porous matrix to effectively trap and detect *E. coli* bacteria from fluids. The new platform thus serves as a low-cost porous substrate to isolate and detect bacteria from fluids.

Acknowledgements

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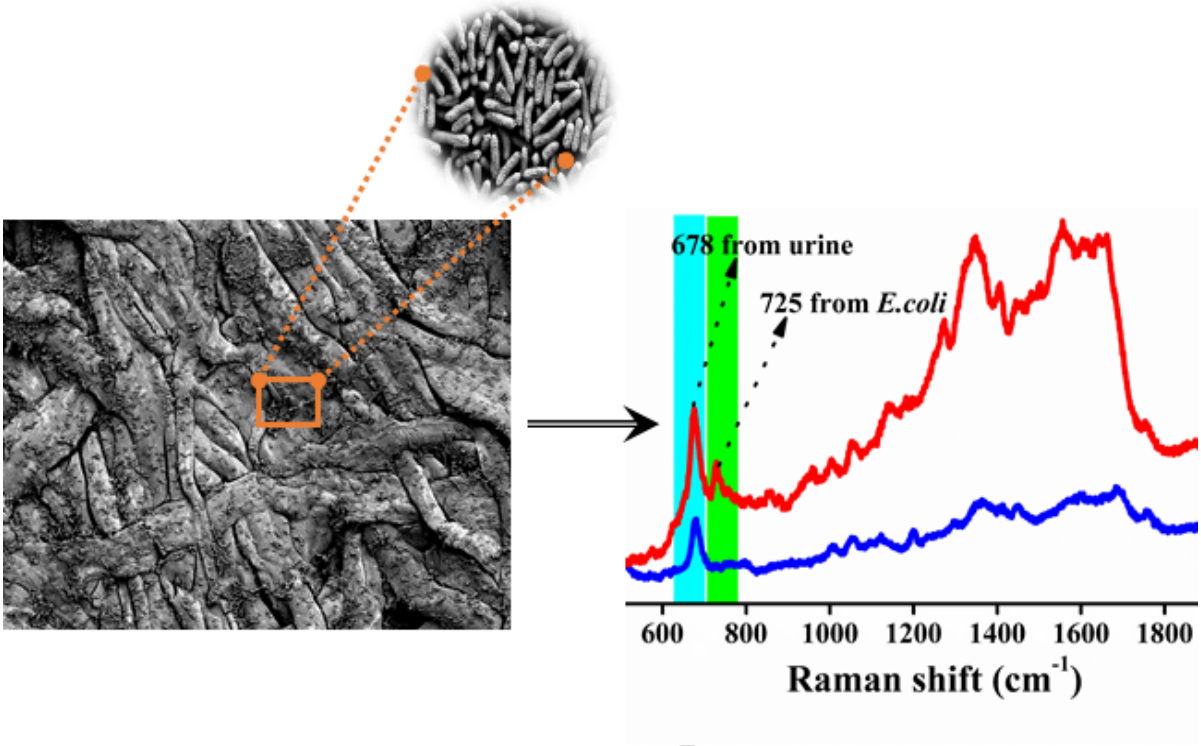

Graphical abstract

HIGHLIGHTS

- Silver nanowires decorated cotton fiber SERS substrate is reported.
- The substrate can be compressed into a filter-like material using a hydraulic press.
- The substrate can be used to trap and detect bacteria from water and urine.