

Fabrication of SERS Swab for Direct Detection of Trace Explosives in Fingerprints

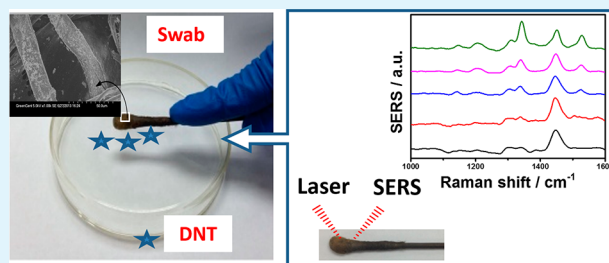
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S Supporting Information

ABSTRACT: Swab sampling is of great importance in surface contamination analysis. A cotton swab (cotton Q-tip) was successfully transformed into surface-enhanced Raman scattering (SERS) substrate (SERS Q-tip) through a bottom-up strategy, where Ag NPs were first self-assembled onto the Q-tip followed by in situ growing. The capability for direct swab detection of Raman probe Nile Blue A (NBA) and a primary explosive marker 2,4-dinitrotoluene (2,4-DNT) using the SERS Q-tip was explored. It was found that at optimum conditions, a femotogram of NBA on glass surface could be swab-detected. The lowest detectable amount for 2,4-DNT is only ~ 1.2 ng/cm² (total amount of 5 ng) on glass surface, 2 orders of magnitude more sensitive than similar surface analysis achieved with infrared technique, and comparable even with that obtained by ion mobility spectrometry–mass spectrometry. Finally, 2,4-DNT left on fingerprints was also analyzed. It was found that SERS signal of 2,4-DNT from 27th fingerprint after touching 2,4-DNT powder can still be clearly identified by swabbing with the SERS Q-tip. We believe this is the first direct SERS swabbing test of explosives on fingerprint on glass. Considering its relative long shelf life (>30 d), the SERS Q-tip may find great potential in future homeland security applications when combined with portable Raman spectrometers.



1. INTRODUCTION

The acts of terrorism and illegal drug trade pose serious challenges to modern society.¹ To tackle these issues, various techniques and methods for the detection of explosives and narcotics have been proposed and deployed. Traditionally, X-ray-based instruments and trained animals are the basic choices to detect these chemicals.² Recently, various techniques, including gas chromatography,³ ion mobility spectrometry, terahertz spectroscopy, and chemical and electrochemical sensors, have been reported for the detection of (trace) explosives.¹

Currently, the most widely adopted sampling methods are wipe/swab sampling and vapor collection sampling for trace explosive analysis.^{4,5} In the case of wipe sampling, normally a wipe pad is supplied. On the other hand, for vapor collection, vacuuming is performed to collect airborne vapor or particles. It is believed that wipe sampling method has better sensitivity. In fact, swab sampling is considered to be one of the most important sampling methods for surface contamination analysis due to its practicality and efficiency, such as virus on food,⁶ bacteria on mechanical ventilator⁷ and textiles,⁸ gun powders,⁹ and explosives.⁴

In recent years, surface-enhanced Raman scattering (SERS) has become one of the most important spectroscopic methods for trace analytes. The advantage of SERS are 2-fold: it is the only optical technique that can both give the quantitative and qualitative information on a minute amount of analytes (down

to single molecules), and the SERS instrument can be miniaturized to fulfill field missions without sacrifice in performance.¹⁰ Thus, it is believed that it is a perfect match for SERS and homeland security. For example, trinitrotoluene and 2,4-dinitrotoluene (2,4-DNT) in solution have been detected at 0.1–0.05 ppt, while the limit of detection (LOD) for a liquid explosive hexamethylene triperoxide diamine (HMTD) is 1 ppm.¹¹ However, much of the current effort has been directed into the developing of sensitive and reproducible SERS substrates.^{11–13} Sampling, one of the key factors in successful detection of trace explosives, has been surprisingly neglected in SERS community. Almost all these SERS substrates are coinage metallic NPs suspensions and NPs on some sort of solid support¹¹ or coinage metallic thin films on rigid substrate fabricated by physical and chemical methods. Apparently, these substrates are not compatible with physical swabbing.¹⁴ As a result, analytes, including explosives, must be collected and dissolved in certain solvents before applied on the SERS substrates. This will inevitably sacrifice the potential of SERS technique to be used in on-site screening applications, such as in homeland security.

Very recently, researchers, including our group, started to develop soft and flexible SERS substrates that might be suitable

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for swab sampling.^{15–21} Gold nanorods have been loaded onto filter paper^{14,18,22} and electrospun polymer nanofibers^{17,23} as flexible SERS substrates. Swab sampling was performed, and it was found that 140 pg of 1,4-benzenedithiol residue spread over 4 cm² surface area could be detected.¹⁸ Inkjet-printed NPs on filter paper¹⁵ and cellulose paper²⁴ have also been developed for the swab detection of Rhodamine 6G, pesticide, and narcotics. polydimethylsiloxane (PDMS) elastomer²⁵ that adsorbed silver or gold NPs was used to image methylene blue adsorbed on gold surface. We reported the fabrication of sandpaper-based²⁰ and hydrogel-based²¹ SERS substrates and their application for swab detection of pesticide on fruit and glass surface, respectively. However, most of these reported substrates only addressed sample analytes, such as Raman dyes^{24,26} and thiols.¹⁸ In addition, extra caution may be needed when using these substrates for swabbing, since the operator needs to hold the substrate with his/her hand directly, and potential risk of damaging the substrate exists.^{15,18}

Swabs made of cotton and polyester have been widely used for the collection of explosives^{27,28} and various pesticides on fruit^{29,30} and fruit peels³¹—in combination with mass spectrometer. It is found that in addition to sample collecting efficiency,⁴ the deploying of swab can not only decrease the sample preparation time but also analysis time.²⁹ However, we are not aware of any reports of building SERS-active swabs for the direct analysis of explosives or any other interested targets, despite the numerous potential advantages that Q-tip-based SERS substrate could bring. Here in this work, we show that by self-assembly of Ag NPs onto a cotton swab, followed by in situ enlarging, a cotton swab can be successfully transformed into a SERS Q-tip. A femotogram of Raman probe Nile Blue A (NBA) spilled on glass can be collected directly with the SERS Q-tip and clearly identified. The LOD for swab detection of 2,4-DNT, a primary explosive marker,³² on glass was found to be 5 ng (spread on ~4 cm², corresponding to ~1.2 ng/cm²). This is 2 orders of magnitude lower than that reported in literature,¹ where the LOD for DNT on metal surface is 220 ng/cm² by using fiber optic coupled absorption/reflection infrared spectroscopy. It is also superior compared with work performed on ion mobility spectrometry (IMS) equipped with mass spectrometer (IMS-MS),³³ where 10 ng of 2,4-DNT was dripped on Nomex swab for detection. Fingerprints on glass obtained after staining with 2,4-DNT powder were examined and even after the 27th touch, 2,4-DNT SERS signal can still be clearly identified by direct swab sampling. The shelf life of the proposed Q-tip based SERS substrate was also examined, and no observable deterioration was found for at least 30 d in ambient air.

2. EXPERIMENT DETAILS

2.1. Materials. All chemicals (silver nitrate (99%), sodium citrate (99%), (3-aminopropyl)trimethoxysilane (APTMS), cetyltrimethylammonium bromide (CTAB), sodium borohydride, Nile Blue A, Rhodamine 6G (R6G), and 2,4-DNT were from Sigma-Aldrich. Cotton swab was bought from local drugstore. Ultrapure water with a resistivity of 18.2 MΩ cm (Nanopure, thermo Scientific) was used in all experiments. NBA solution was prepared by dissolving appropriate amount of NBA solid in EtOH followed by stepwise dilution with same solvent. For 2,4-DNT, the solvent used was acetone.

2.2. Instruments. An UWave-1000 microwave (Sineo Microwave, Shanghai) was used to synthesize the Ag NPs. Raman measurements were performed on customized Raman microscope equipped with Pixis-100BR CCD, Acton SP-2500i spectrograph and 20 mW He–Ne laser. Raman mapping was performed on Renishaw InVia Raman

microscope. Unless otherwise mentioned, 20× objective (N.A. = 0.45) was used to focus the laser directly onto the SERS Q-tip. Sonication was performed on a temperature-stabilized triple frequencies ultrasonic cleaner (Model KQ-300GVDV, Kunshan Ultrasonic Ltd. Co., China). Scanning electron microscope (FE-SEM, Hitachi S-4800) was used to observe the morphology of SERS Q-tip.

2.3. Preparation of Ag NPs. Microwave reactor was used to synthesize Ag NPs. First, 600 mL of AgNO₃ solution (5 mM) was heated to 98 °C under vigorous stirring within 15 min, then 12 mL of 10% sodium citrate solution was quickly added, and the solution was kept at 98 °C for 30 min. After that, stirring was kept until the solution was cooled to room temperature. The ultrasonic power was 100 W, and stirring speed was 800 r/min.

2.4. Decoration of Cotton Swabs. For optimization of the performance of substrate, three different fabrication protocols were implemented as follows:

2.4.1. Ag NPs Self-Assembly. The cotton swabs were modified according to literature.³⁴ Briefly, a 2% APTMS solution was prepared using ethanol/water (95:5 v/v) mixture as solvent. The cotton swabs were immersed in the solution for 30 min under ultrasonic agitation. After that, the swabs were removed from the solution and thoroughly rinsed with ethanol, followed by incubation in oven at 120 °C for 20 min to activate the fiber. Later, the swabs were rinsed with ethanol and water successively. Finally, the swabs were soaked in Ag NPs solution for 30 min under sonication. The Ag NPs-modified cotton swabs were then cured at 120 °C in N₂ atmosphere for 1 h.

2.4.2. In Situ Growing.^{35,36} The cotton swabs were dipped in CTAB solution (1% w/w) for 5 min under ultrasonic agitation before rinsing with pure water. Then, the swabs were immersed in AgNO₃ solution (100 mM) under sonication for 30 min, followed by rinsing with ethanol. Later, the swabs were soaked in NaBH₄ solution (50 mM) for 10 min with ultrasonic agitation. Finally, the swabs were cured at 120 °C in N₂ atmosphere for 1 h.

2.4.3. Combination of Self-Assembly and in Situ Growing. This procedure was the combination of approaches in Sections 2.4.1 and 2.4.2. The swabs were first modified according to the procedure in 2.4.1 but without curing. Then, procedure in 2.4.2 was applied.

2.5. Swab Sampling on Surfaces. The swab detection was performed as follows: to a glass slide, an appropriate volume of sample solution at given concentration was dropped on. After the evaporation of solvent, for NBA, 20 μL of ethanol was supplied followed by wiping with the SERS Q-tip. For 2,4-DNT, the solvent supplied was acetone.²⁷ Note that in case of 2,4-DNT swabbing, the SERS Q-tip was first soaked in 10 mM NaOH for 1 min for better attraction of the explosive.³⁷

Swab detection of 2,4-DNT-contaminated fingerprints: to simulate the real-world application, 2,4-DNT was first ground into powder in a weighing boat. Glass was rinsed with EtOH and dried in air. After touching the 2,4-DNT powder with hand, fingerprint was continuously pressed onto the glass and labeled with number. Note: to make sure the pressure is the same, glass slide was left on a top loading scale, and the reading was kept to ~1 kg when pressing. To collect the 2,4-DNT powder on fingerprints on glass slide, 50 μL of acetone²⁷ was used as solvent to wet each fingerprint before swabbing with the SERS Q-tip, respectively.

2.6. SERS Measurements. All the Raman measurements except mapping results were performed on customized Raman microscope using 632.8 nm laser as excitation source. At least 10 spots on the same Q-tip were examined, and the spectra were collected and averaged for a given single SERS spectrum.

3. RESULTS AND DISCUSSION

3.1. Optimization of the SERS Swab. We first evaluated the SERS performance of the three substrates. Ten microliters of Raman probe NBA ethanolic solution (1 ppm) was dripped on the swabs. Raman spectra were recorded after the evaporation of solvent. Note that the laser wavelength used in this work falls into the absorption range of NBA. Thus, the spectra for NBA are so-called surface-enhanced resonance

Raman scattering (SERRS). Also note that high laser power shall be avoided for this specific Raman probe since it can be photobleached. Figure 1 shows the SERRS spectra obtained

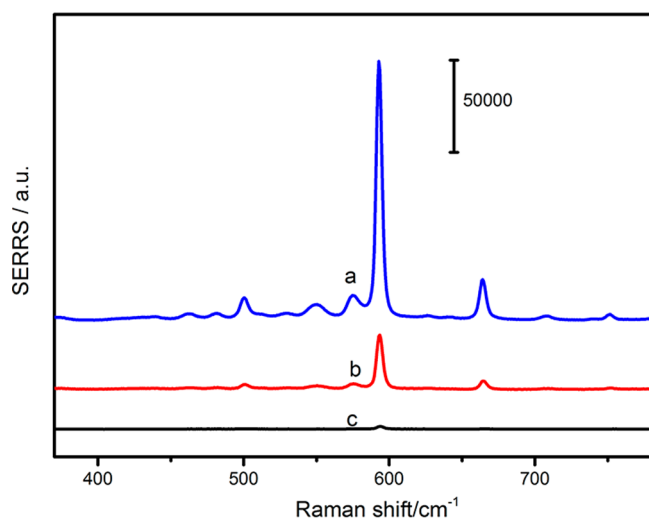


Figure 1. Comparison of SERS performance of the SERS Q-tip fabricated through different protocols. Integration time $50 \text{ ms} \times 5$, laser power, $300 \mu\text{W}$. From a to c: self-assembly combined with in situ synthesis, in situ synthesis, and self-assembly, respectively.

from the as-prepared substrates. It is clear that SERS Q-tip fabricated with combination of self-assembly and in situ enlarging has highest sensitivity.

This can be rationalized by the SEM images shown in Figure 2, where the morphology of silver on the cotton fiber was shown. The self-assembly process (Figure 2B) only brought scattered Ag NPs onto the cotton fiber, which is probably due to the short deposition time in the protocol. This is also in agreement with our previous works;^{38–41} however, this kind of one-time-deposition is not enough to gather sufficient Ag NPs, that is, SERS hot spots,¹³ onto a solid substrate. As a result, the SERS signal from substrate made from this protocol is the weakest (Figure 1c). On the other hand, the in situ growing procedure (Figure 2C) adapted from literature^{35,36} formed micrometer-sized continuous silver islands on the fiber. We believe both the high concentration of AgNO_3 and the physical agitation from ultrasound contributed to the observed large features.³⁶ However, this kind of large feature is inefficient in Raman signal enhancement.⁴² In turn it is natural that substrate made from this latter protocol only showed moderate improvement (Figure 1b), even though the coverage of Ag NPs on the fiber surface is much larger compared with the substrate obtained through self-assembly process. Finally, the combination of the two protocols (Figure 2D) gave a densely packed Ag NPs (aggregates) whose sizes were less than 100 nm

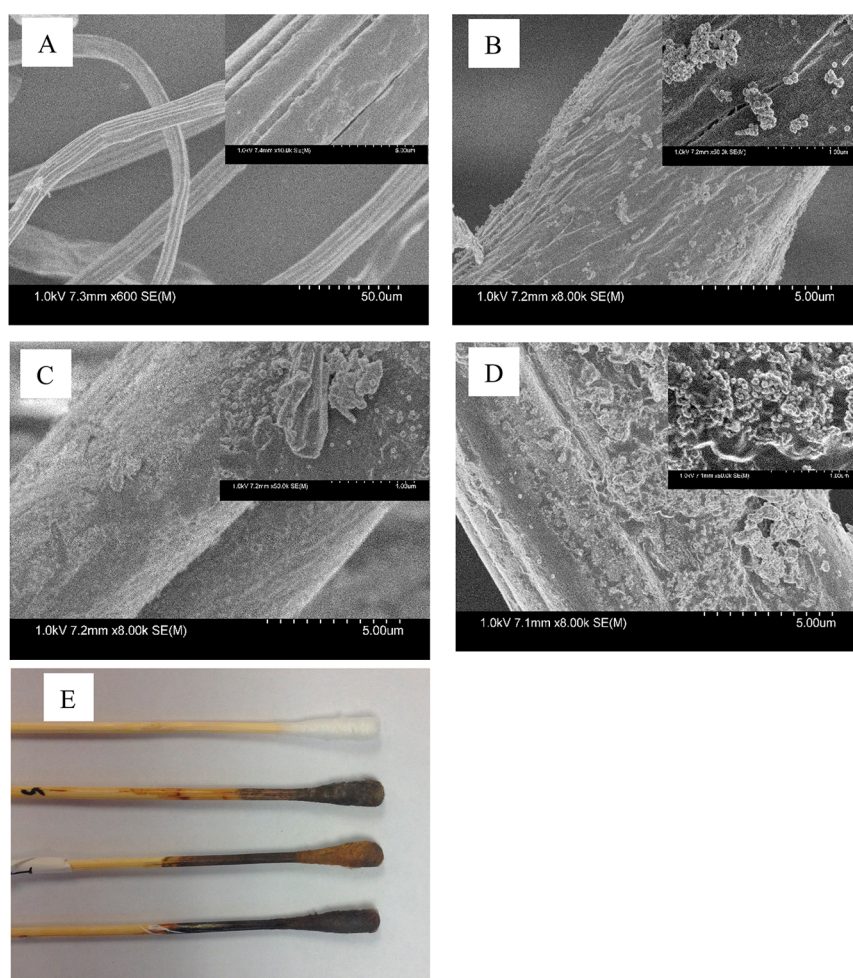


Figure 2. SEM images of: (A) blank Q-tip; (B) Q-tip with self-assembled Ag NPs; (C) Q-tip with in situ growing Ag NPs; and (D) Q-tip with first self-assembly then in situ enlarging Ag NPs; (E) optical images of A to D (top to bottom).

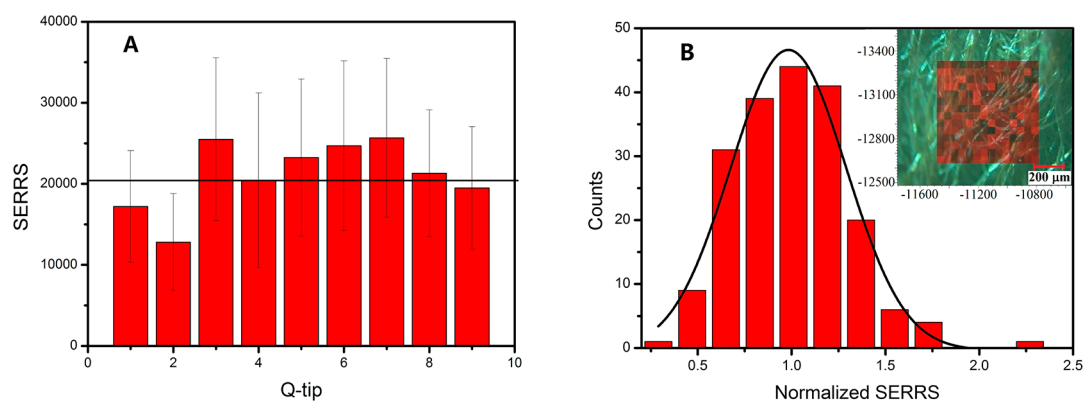


Figure 3. (A) The reproducibility of the SERS Q-tips. The transverse line shows the average SERS intensity from nine swabs, and the error bar indicates the signal derivation within single swab (20 spots). Integration time 50 ms \times 5, laser power 95 μ W. (B) Statistic of a SERS mapping of a single swab. (inset) The optical image and the SERS map. The scale bar represents 200 μ m. Laser power 600 μ W, integration time 300 ms, objective used was 5 \times .

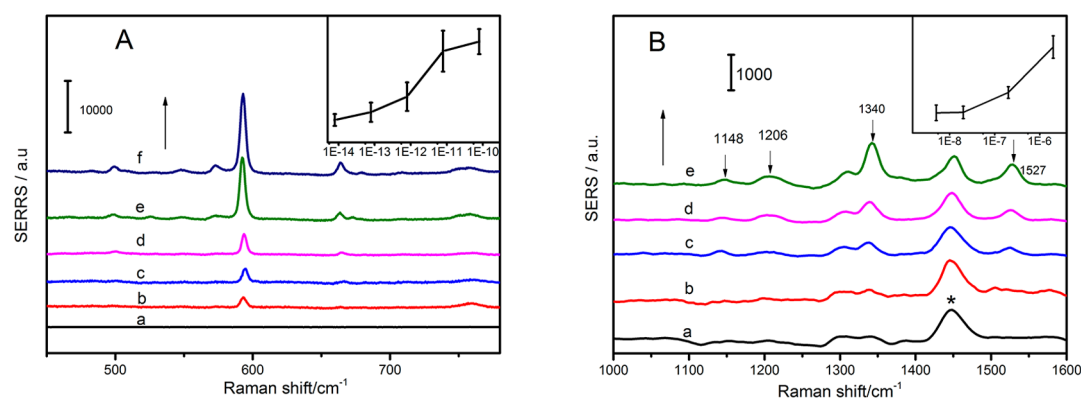


Figure 4. (A) SERS spectra of NBA at different concentrations, sample volume 10 μ L. Integration time 1 s \times 20, laser power 95 μ W. Spectra *a* to *f* were: 0, 0.1 ppt, 1 ppt, 10 ppt, 100 ppt, 1 ppb, respectively. (inset) The plot of SERS intensity at 593 cm^{-1} vs the total amount of analyte in grams. (B) SERS spectra of 2,4-DNT at different concentrations. Note each spectrum is an average of a map on the SERS Q-tip performed on Renishaw inVia system. Sample volume 20 μ L. Integration time 1 s, laser power, 3.2 mW. Objective 5 \times . Spectra *a* to *e* were 0, 0.25, 1, 10, and 100 ppm, respectively. (inset) The plot of SERS intensity at 1340 cm^{-1} vs the total amount of analyte in grams. Asterisk in *b* indicates the band from substrate (CTAB⁴⁵).

and full of cavities. We believe that the self-assembled NPs acted as seeds, provided the anchor points for further in situ growth in the following step, and hence gave the observed morphology. This kind of densely packed Ag NPs structure is known to be associated with very high SERS performance.^{12,13,42} Thus, it is not surprising that the last protocol gave the highest SERS efficiency (Figure 1a) compared with the other two protocols.

Figure 2E is the image of the cotton swabs after respective modification procedures. It is further showing that distinctive morphology formed through the three protocols. For the swabs underwent self-assembly procedure, it is dark yet white cotton color can still be found, indicating the coverage is not enough. On the other hand, after in situ growing the swab presents brown color. Finally, the combination of the two procedures gives dark brown color, indicating different nanomaterial morphology compared with that from in situ growing only. These are in agreement with what are shown in Figure 2B–D. Thus, the swabs used in the following section are fabricated by the optimized approach, that is, self-assembly of Ag NPs followed by in situ growing.

The SERS enhancement factor (EF) was also estimated according to literature,⁴³ where the following formula and molecular probe R6G was used:

$$EF = \left[\frac{I_{\text{SERS}}}{I_{\text{Raman}}} \right] \times \left[\frac{N_{\text{Raman}}}{N_{\text{SERS}}} \right] \times \left[\frac{P_{\text{Raman}}}{P_{\text{SERS}}} \right] \times \left[\frac{T_{\text{Raman}}}{T_{\text{SERS}}} \right]$$

where the parameters *P* and *T* represented the laser power and the acquisition time, respectively. The Raman band used was the strongest one at 1509 cm^{-1} , and the calculated SERS EF was found to be 1.6×10^6 , which falls into the average range of typical SERS substrate.¹³

3.2. Reproducibility of the SERS Swab. While high sensitivity is our primary objective in SERS swab development, it is also important to examine its reproducibility. To do this, SERS Q-tips were prepared and dipped into 1 ppm of NBA ethanolic solution for 30 s. SERS spectra were recorded on 20 different points on each single swab after evaporation of solvent. As shown in Figure 3A, the RSD% ranges from 36% to 52% within a SERS Q-tip. However, the statistic on average SERS intensity among different SERS Q-tips showed acceptable variation (\sim 20%). This is comparable with our former work.⁴⁰ In Figure 3B, a SERS mapping was performed on a SERS Q-tip using a Renishaw inVia Raman microscope system. The SERS signal falls into a Gaussian distribution with \sim 30% of RSD, probably because larger laser spot presented when using 5 \times objective, which was known as an effective way of minimizing signal variation in SERS.⁴⁴ Most

importantly, a close examination of the SERRS map and optical image found that the SERS hotspots came from fiber joints. This is not surprising, since close-packed NPs provide best SERS efficiency.¹³

3.3. Swab Detection of NBA and 2,4-DNT. For the SERS sensitivity evaluation in swab sampling of the SERS Q-tip, we tested both dye probe NBA and explosive 2,4-DNT (Figure 4). As can be seen in Figure 4A, the characteristic SERRS peak for NBA at $\sim 593\text{ cm}^{-1}$ can still be clearly identified even when the concentration is only 0.1 ppt. Considering the small volume used ($10\ \mu\text{L}$ of ethanolic solution), there is only 0.78 fg of analyte. We believe this is the lowest LOD in literature for this kind of swab analysis to the best of our knowledge,¹⁵ 3 orders of magnitude more sensitive compared with our previous work using SERS slime.²¹ We also tested explosive 2,4-DNT, and the results are shown in Figure 4B. It is clear that even at 250 ppb with the total volume of $20\ \mu\text{L}$, which equals an amount of 5 ng on the contaminated surface, the most dominant SERS fingerprint of 2,4-DNT at 1340 cm^{-1} can still be clearly identified. Since the contaminated surface is $\sim 4\text{ cm}^2$, the calculated surface density of 2,4-DNT is only $\sim 1.2\text{ ng/cm}^2$. It is 2 orders of magnitude lower than what was achieved by the use of fiber optic coupled absorption/reflection infrared spectroscopy on metal surface.¹ Meanwhile, this is the first direct SERS swab test of explosives to the best of our knowledge. Furthermore, considering the LOD of 2,4-DNT is 10 ng on similar swab test but performed on ion mobility spectrometry (IMS) equipped with mass spectrometer (IMS-MS),³³ apparently our work shows great advantage due to potential applications in field analysis when combining with portable Raman spectrometers.

3.4. Swab Detection of 2,4-DNT on Fingerprints. Swabbing the surfaces for sample collection is a strategy extensively employed in passenger screening at many security check points. After evaluating the SERS performance of the as-prepared SERS Q-tip, as a proof of concept, in this section we will demonstrate that it can be applied for the direct swab detection of 2,4-DNT. As explained in the Experimental Section, sequential fingerprints were pressed on glass after touching 2,4-DNT. By wetting the surface with $50\ \mu\text{L}$ of acetone, swab detection with the SERS Q-tip was performed. Figure 5 shows the results of blank (no 2,4-DNT), ninth, 16th, 23rd, and 27th of touching with contaminated finger, respectively. It is clear that even after 27th touch, the characteristic bands of 2,4-DNT are still clearly visible. Note that, because of the nature of pressing, the amount of 2,4-DNT on the glass surface is not linearly changing with touching/pressing sequence. Thus, there is no linear response of SERS intensity of 2,4-DNT. However, the experiments shown in this section clearly indicate the promising prospect of applying our SERS Q-tip in homeland security.

CONCLUSION

In conclusion, we have demonstrated the fabrication of sensitive and cost-effective SERS Q-tip based on self-assembly of Ag NPs followed by in situ growing silver on commercial cotton swab. Thanks to the good collection efficiency inherited from the swab and high SERS sensitivity from the dense Ag NPs on cotton fiber, the LOD for the swabbing detection of Raman probe NBA on glass surface is only 0.78 fg. The LOD for explosive 2,4-DNT on glass was found to be 5 ng ($\sim 1.2\text{ ng/cm}^2$), 2 orders of magnitude more sensitive than what was reported in literature achieved on metal surface by infrared

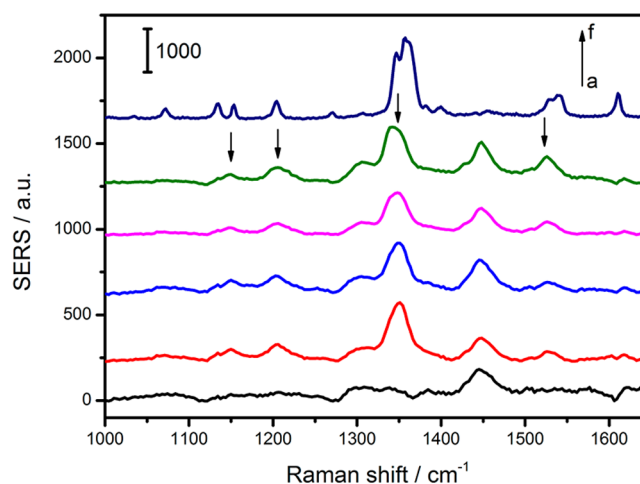


Figure 5. SERS spectra of 2,4-DNT obtained by swabbing fingerprint on glass. Integration time $1\text{ s} \times 20$, laser power $500\ \mu\text{W}$. Spectra a to e were blank, 6th, 13th, 19th, and 27th of pressing with 2,4-DNT contaminated finger. Line f is the normal Raman of 2,4-DNT as reference.

spectroscopy, and comparable to similar situation with IMS-MS. Furthermore, swab test of explosive residual on fingerprint after as many as 27 times of contact with glass is achieved. We believe this is the first direct SERS explosive swab test on fingerprint in literature. Although the tested surfaces are limited in this work, as a proof of concept, we believe the SERS Q-tip can be a potential powerful tool in trace analysis in homeland security and crime scene investigation when combined with portable Raman spectrometers.

ASSOCIATED CONTENT

Supporting Information

Raman spectra of SERS maps and graph showing shelf life of SERS Q-tip. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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