

# Au-NP-Decorated Cotton Swabs as a Facile SERS Substrate for Food-Safety-Related Molecule Detection

Farzana Rafiq, Ning Wang, Keyou Li, Zijin Hong, Dandan Cao, Jingjing Du, and Zhenli Sun\*

Cite This: *ACS Omega* 2023, 8, 8541–8547

Read Online

ACCESS |



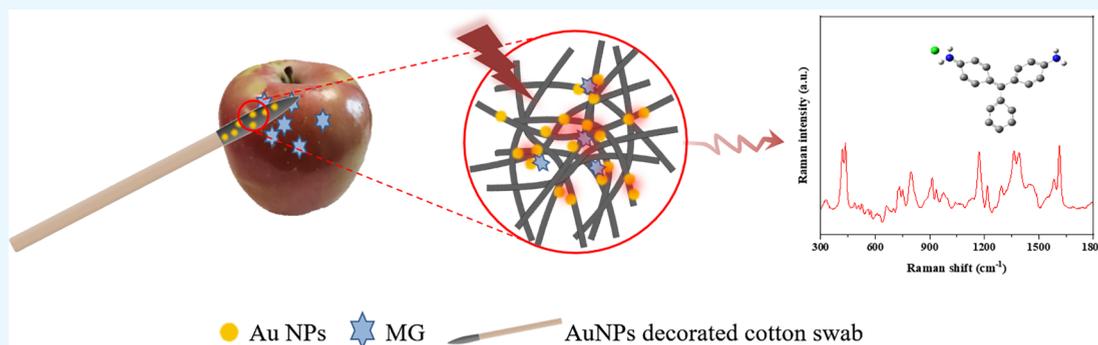
Metrics &amp; More



Article Recommendations



Supporting Information



**ABSTRACT:** Recently, food safety has received considerable attention, and various analytical techniques have been employed to monitor food quality. One of the promising techniques in this domain is the surface-enhanced Raman scattering (SERS) technique. This study developed a facile, cost-effective SERS method by supporting a wipe-type substrate with a small-head cotton swab. We fabricated Au-nanoparticle (NP)-decorated cotton swabs (CS-Au NP) via the dropwise addition of gold colloid on the cotton fibers. These swabs exhibit reduced gold colloid consumption and a compact fiber structure, allowing for the uniform distribution of Au NPs and easy capture of molecular signals. Experiments were conducted to obtain a CS-Au NP wiper performance optimized for cotton swab selection, NaCl concentration, and Au NP layers. The Raman reporter molecule 4-mercaptopyridine was detected at a concentration of  $1 \times 10^{-8}$  M and a relative standard deviation of  $\leq 10\%$ . The proposed SERS platform enables the facile and reliable detection of food-safety-related molecules such as malachite green on the surface of fruits and vegetables. This paper describes the development of an easy, cost-effective, and environment-friendly method of detecting food-safety-related molecules on various food surfaces through SERS.

## 1. INTRODUCTION

Recently, food safety has been a growing concern. Several chemicals for food processing have been established over the past 50 years owing to advancements in food science and technology.<sup>1</sup> Fruit and vegetable pesticide residues pose a global threat to the environment and public health.<sup>2</sup> These chemicals are present in daily diet items such as vegetables, fruits, meat, and fish, resulting in the development of several pesticide detection methods to test the level of contamination before consumption. Commonly used pesticide analysis methods include mass spectroscopy,<sup>3</sup> enzyme-linked immunosorbent assay,<sup>4</sup> and liquid chromatography.<sup>5</sup> Furthermore, pesticide residues have been detected using fluorescence and Fourier-transform infrared spectroscopy techniques in agriculture, aquaculture, and food samples.<sup>6,7</sup> However, these techniques have drawbacks, such as heavy instrumentation, complexity in sample preparation, poor reproducibility, reliability, and time-consuming processes. Therefore, easy, quick, sensitive, and reliable analytical approaches are needed for detecting harmful pesticides in food samples.

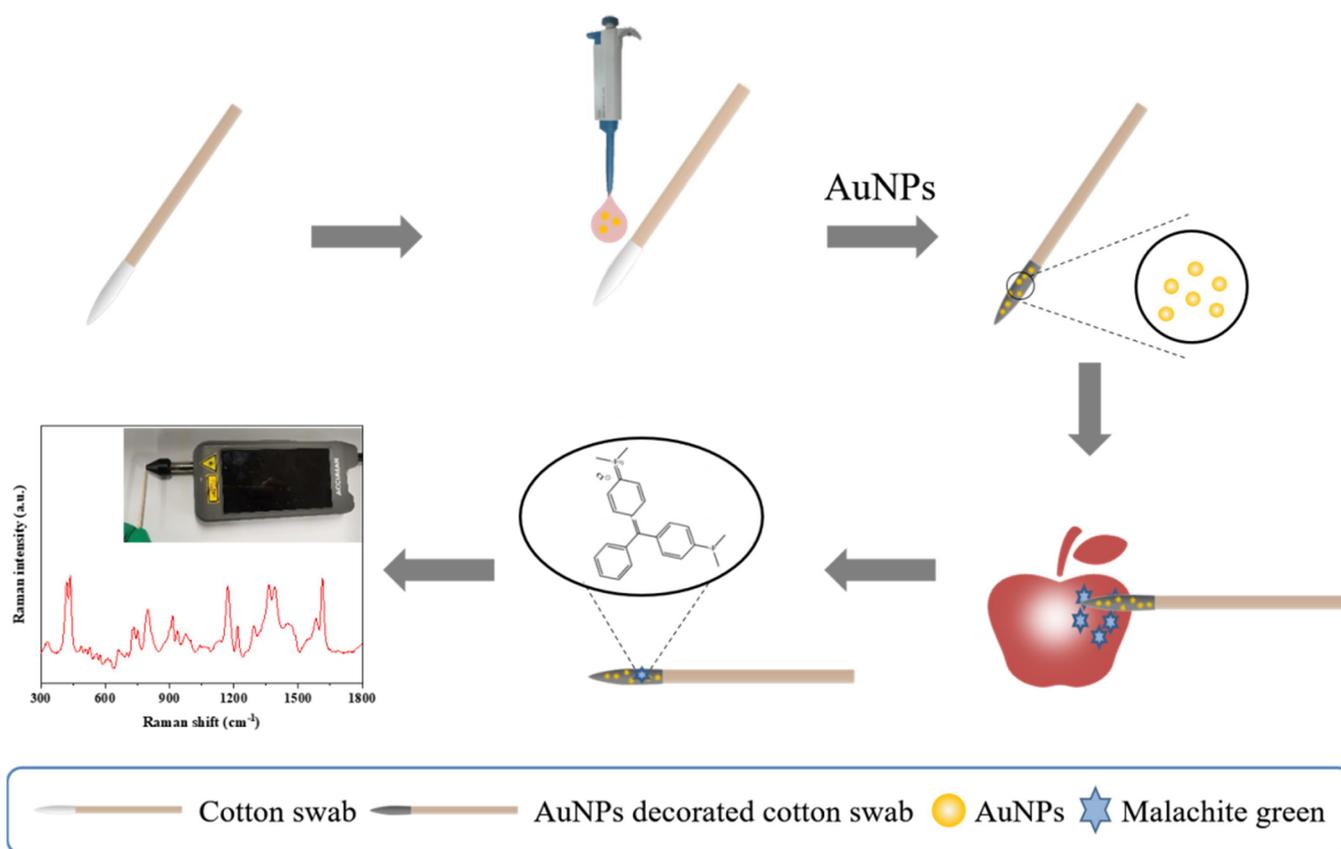
Surface-enhanced Raman scattering (SERS) has been widely used to detect pesticide residue in food and agricultural products.<sup>8,9</sup> The SERS technique entails the detection of substrate signals with high sensitivity, simple sample production, and non-destructive sample analysis.<sup>10–12</sup> Recently, several plasmonic nanomaterials, such as Si-based Au nanowires,<sup>13</sup> glass-based Ag films,<sup>14</sup> and two-dimensional MXene nanosheets of Ag-based composite,<sup>15</sup> have been proposed and used for the pesticide monitoring of food samples using SERS. These solid substrates exhibit excellent uniformity and recyclability.<sup>16</sup> However, they are usually rigid and unsuitable for detecting pesticide residues on complex surfaces. On the other hand, flexible SERS substrates exhibit

Received: December 1, 2022

Accepted: January 24, 2023

Published: February 23, 2023





**Figure 1.** Fabrication of the SERS substrate and detection of chemicals on a fruit surface.

significant shape variability, have sizes suitable for on-demand use, and enable the rapid wiping of complex surfaces of various actual analytes (wipe sampling) for efficient and convenient SERS detection. Such flexible SERS substrates have been widely used in food safety.<sup>16,17</sup>

Various materials, including cellulose fiber, paper, polymers, and cotton fabrics, have been used to create flexible SERS substrates.<sup>18–21</sup> In particular, cotton-swab-based substrates have been widely studied owing to their easy handling, strong fibers, and flexibility. Cheng et al.<sup>22</sup> synthesized flexible SERS substrates by isolating Ag@Au NPs on the surface of cotton fabrics to detect carbaryl insecticides on cucumber using a synthetic procedure that required approximately 2 days. Kong et al.<sup>23</sup> fabricated Ag-NP-modified cotton swabs by immersing cotton swabs coated with sodium chloride (NaCl) in Ag colloids to detect pesticide residues. The modification of the substrate surface by metal colloids can increase the absorption capacity of the substrate, which can assist in the improved detection of pesticides. These substrates are simple to prepare and flexible in application. However, an SERS substrate supported by traditional cotton swabs typically consumes a substantial amount of metal colloids. The complicated fiber structure makes signal capture or inhomogeneity difficult, rendering the process expensive or inefficient. Improving the performance of SERS substrates by optimizing the dimensions of the nanoparticles and the substrate preparation method is essential.

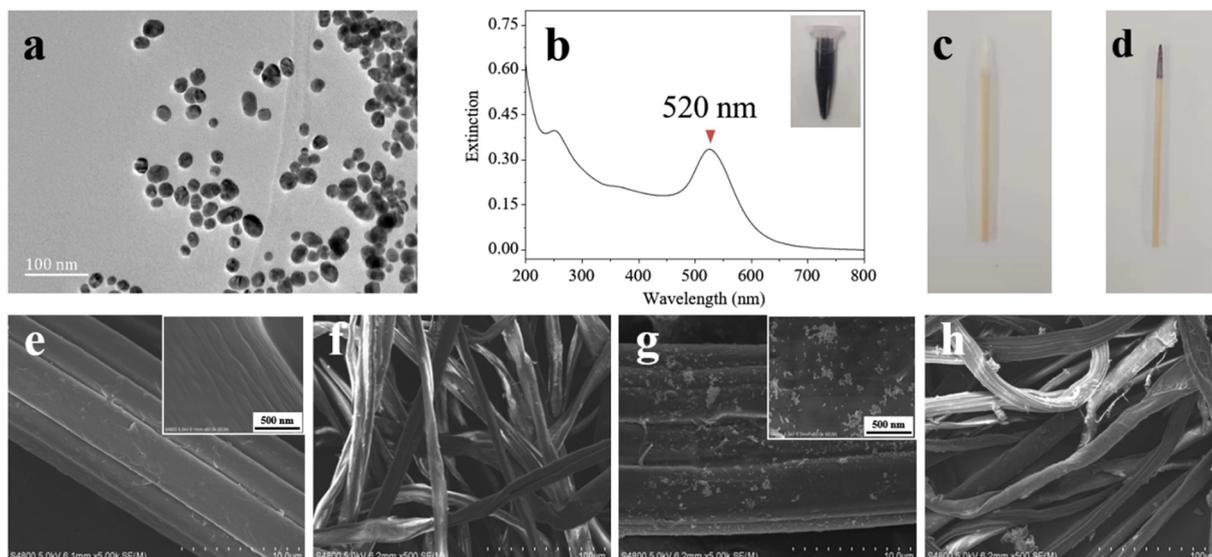
In this study, we chose small-head cotton swabs as the support and synthesized highly sensitive Au-NP-decorated cotton swab (CS-Au NP) substrates. Furthermore, we effectively utilized the swabs for the SERS detection of

malachite green (MG) and 4-mercaptopyridine (4MPY). The as-prepared CS-Au NP substrates were highly cost-effective as they used less gold colloid owing to their small-sized heads. The absorption and detection limits (LOD) of the CS-Au NP substrate were enhanced by varying the gold content in the substrate. Furthermore, using the wiping method, the synthesized SERS swabs were utilized as flexible SERS substrates to detect MG residues in apples, grapes, bottle gourds, and bitter gourds. Therefore, CS-Au NP substrates can act as highly promising and efficient substrates for the on-site detection of trace pesticide residues in food.

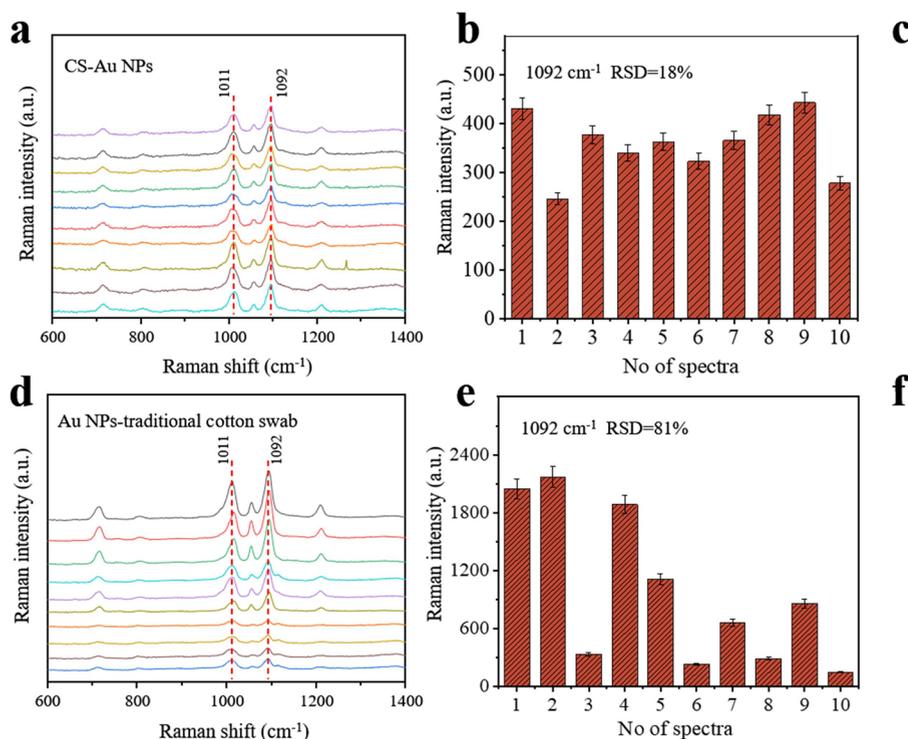
## 2. MATERIALS AND METHODS

**2.1. Chemicals and Equipment.** Sodium citrate (Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>, 98%) was purchased from Aladdin Biochemical Technology, and 4-mercaptopyridine (4MPY, 97%), was obtained from the Tansoole Platform. NaCl, MG (C<sub>23</sub>H<sub>25</sub>N<sub>2</sub>), and chloroauric acid (HAuCl<sub>4</sub>·4H<sub>2</sub>O) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Cotton swabs, bitter gourds, grapes, and apples were acquired from a local market in Beijing. Deionized water (H<sub>2</sub>O) was used to prepare all solutions.

All SERS spectra were acquired directly by a portable Raman spectrometer (SR-510, Ocean Optics, Shanghai, China) with a 785 nm excitation wavelength and a resolution of 4 cm<sup>-1</sup>. The spot size of the detection for their Raman spectroscopy was 100–200 μm. The scanning electron microscope (SEM) images were recorded on a Hitachi S-4800 apparatus. The transmission electron microscopy (TEM) images were obtained by a JEM-2100F (Jeol, Japan) electron microscope.



**Figure 2.** (a, b) TEM and UV–vis spectra of the prepared Au NPs. (c, d) Photograph of the SERS cotton swabs: blank and with the decoration of Au NPs. (e, f) SEM images of the original cotton swabs. (g, h) SEM images of the cotton swabs deposited with one Au layer.



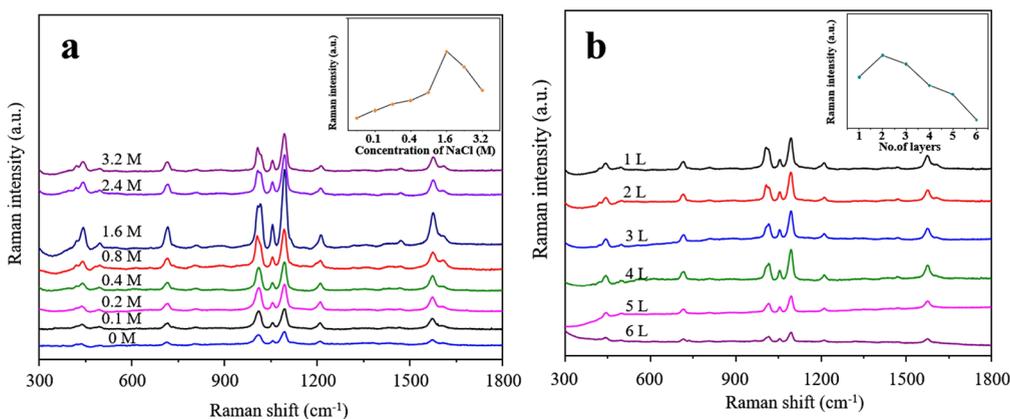
**Figure 3.** Raman spectra of 4MPY ( $10^{-5}$  M) obtained from Au NPs on the (a) small-head swab and (d) traditional cotton swab. (b, e) Histogram of peak intensity at  $1092\text{ cm}^{-1}$  in (a) and (d). (c, f) Schematics of the two substrates in (a) and (d).

The UV–vis spectra were recorded on a SHIMADZU UV-2550 spectrophotometer.

**2.2. SERS Wiper Fabrication.** The Au NPs were prepared by using a previous research method that was modified slightly.<sup>24</sup> Briefly, in a conical flask, 50 mL of  $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$  solution was heated to  $130\text{ }^\circ\text{C}$  by magnetic stirring for 20 min. Following that, 0.2 M sodium citrate solution (2 mL) was mixed to the above solution while it was continuously boiling and stirring. After 20 min, the solution's color changed from yellow to wine red, confirming the formation of Au NPs. To remove excess sodium citrate, the prepared Au NPs were

centrifuged at 2000 rpm for 20 min before use. Each centrifuge tube was filled with 1.5 mL of Au colloid, and 1.4 mL of supernatant was removed after centrifugation. The remaining part of each extractor tube was transferred into a centrifuge tube for the flowing experiment.

The formulation of the SERS swab is based on some modifications from previous literature.<sup>23</sup> First, the cotton swab was washed with deionized water and then immersed in a NaCl solution for 20 min; it was later removed from the NaCl solution and desiccated in an oven at  $60\text{ }^\circ\text{C}$  for 3 min to activate the SERS cotton fiber. After that, a swab was treated



**Figure 4.** (a) Raman spectra of 4MPY ( $10^{-5}$  M) enhanced by SERS wiper fabricated under different concentrations of NaCl (0 to 3.2 M), inserted figure: Raman intensity at  $1092\text{ cm}^{-1}$  illustrated against the NaCl concentrations. (b) Spectra of 4MPY ( $10^{-6}$  M) enhanced by SERS wipers fabricated with 1–6 Au layers. Inserted figure: Raman intensity at  $1092\text{ cm}^{-1}$  illustrated against the number of Au layers.

with pure Au colloid solution to prepare the CS-Au NP substrate.

**2.3. SERS Detection.** Various concentrations (from  $1 \times 10^{-4}$  to  $1 \times 10^{-8}$  M) of 4MPY were prepared, and  $10\ \mu\text{L}$  of 4MPY solution was dropped on CS-Au NP substrates to collect the SERS signal. In the application section,  $20\ \mu\text{L}$  of MG was dropped on the surface of fruits and vegetables. The SERS spectra of MG on fruit surfaces ( $1\text{ cm}^{-2}$ ) was obtained by wipe sampling detection coupled with the fabricated CS-Au NP wiper. The SERS measurement of each sample was performed at least 10 times with an integration time of 3 s and a laser power of 140 mW, and the average value of the calculations was used for subsequent analyses.

### 3. RESULTS AND DISCUSSION

**3.1. Fabrication and Characterization of the CS-Au NPs.** We developed a sensitive CS-Au NPs substrate by dipping a small-head cotton swab into an Au NP colloid as shown in Figure 1. This study used a cotton swab as the supporting substrate because it is composed chiefly of  $\alpha$ -cellulose (98%), which provides rich attachment sites for dense Au NP dispersion. The Au NPs were attached to the cotton swab via adsorption. We anticipated that the compact, sensitive Au-NP-coated head swab would provide several advantages: (1) Consume less gold colloid to reduce costs; (2) Acquire a more uniform signal; (3) Easily capture molecular signals and could be used as a facile wipe-based substrate.

The morphology and structure of the SERS wipers were characterized using TEM, SEM, and ultraviolet–visible spectroscopy (UV–vis) (Figure 2). As shown in Figure 2a, spherical-shaped Au NPs with an average diameter of approximately 20 nm were synthesized in the experiment. Furthermore, UV–vis analysis of the wine-red gold colloid (inset in Figure 2b) showed an absorption peak at 520 nm in the UV–vis spectrum, which also proved the formation of spherical gold NPs with a diameter of 20 nm. Moreover, Figure 2c,d shows the cotton swab appearance before and after Au NP decoration. The cotton swabs changed from white to black after applying the Au colloid owing to the deposition of the Au NPs on the cotton fibers. These findings showed that the Au NPs were successfully immobilized on the fibers. This result was confirmed by the SEM images (Figure 2e–h). The Au NPs were more abundant on these fibers (Figure 2g,h, Figure S1) than on the original cotton swab (Figure 2e,f). These

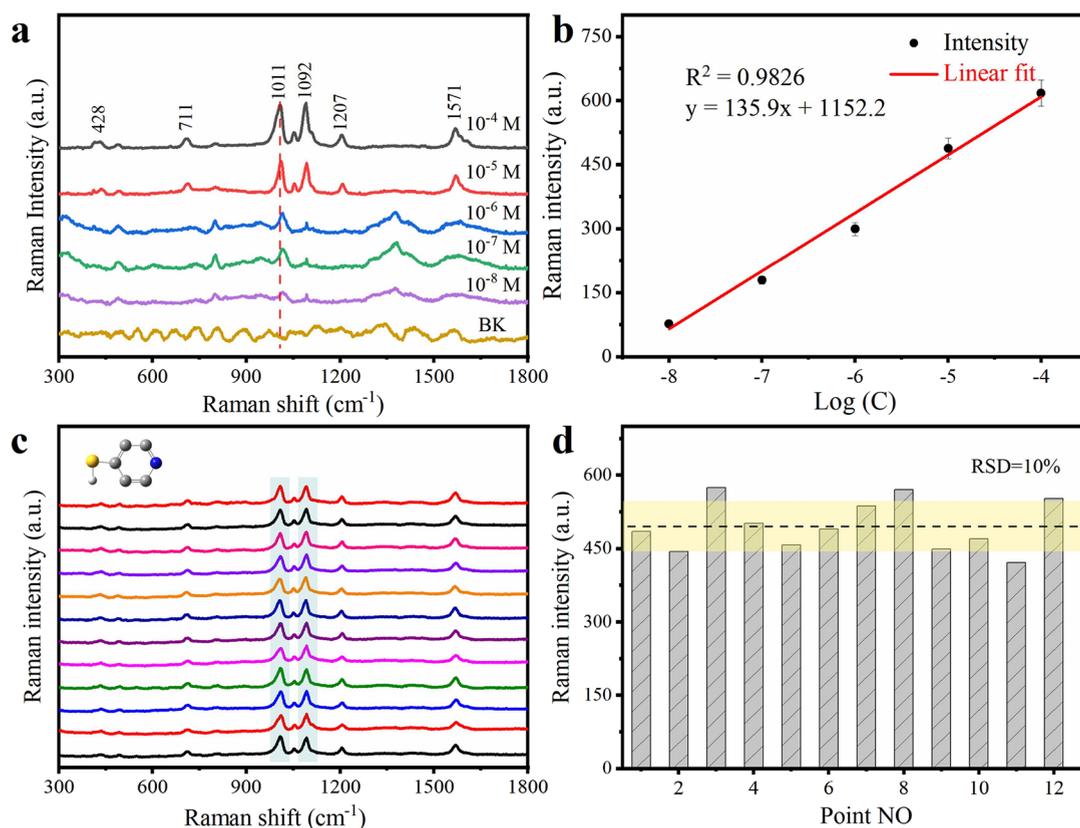
outcomes demonstrate that the CS-Au NPs SERS platform was successfully assembled and thus can be applied for SERS detection.

**3.2. Optimization of the SERS Wiper.** **3.2.1. Optimization of the SERS Wiper.** High sensitivity, high stability, and low cost are the three targets in developing SERS substrates. Two types of flexible cotton swabs (small-head swab and traditional-head swab) were investigated to maximize the SERS performance of flexible cotton swabs. 4MPY was the preferred model probe to assess the feasibility of the proposed SERS substrates. From the experimental results, the SERS spectra exhibited Raman peaks at 428, 711, 1011, 1092, 1207, and  $1571\text{ cm}^{-1}$  (Figure 3a,d). Previous research has established that the breathing ring mode specifies the peak corresponding to 4MPY at  $1092\text{ cm}^{-1}$ , and the pyridine ring C=C stretching modes are responsible for the two peaks of 4MPY at 1207 and  $1571\text{ cm}^{-1}$ .<sup>25,26</sup> The peak at  $1092\text{ cm}^{-1}$  was selected to evaluate the uniformity or sensitivity activity of the small-head-swab and traditional-head-swab SERS substrates (Figure 3b,e).

The relative standard deviation (RSD) of the Raman intensity was obtained at  $1092\text{ cm}^{-1}$  from 10 parallel points encapsulated from one cotton swab. The results show that the RSD was 18% on the small-head swab, whereas on the traditional-head swab, it was approximately 81%. (Figure 3b,e), which can be explained by the denser distribution of Au NPs on the compact fiber structure. Compared with traditional swabs, small-head swabs have a more homogeneous structure owing to the simplicity of their preparation method and the inherent consistency of the swab. The closely spaced fibers on small-head swabs allow for a denser Au NP arrangement on the surface and easier access to molecular signals.

Furthermore, we compared the consumption of the gold colloid in synthesizing substrates supported by either a small-head swab or traditional-head swab. The small-head swab consumes fewer Au NPs, namely, approximately 1/10 of the number of Au NPs consumed by the traditional swab, proving that the small-head swab is economical, as shown in Figure 3c,f and Figure S2. A small-head swab was used in further research considering its excellent properties.

**3.2.2. Optimization of CS-Au NP Performance.** NaCl was used to increase the decorating efficiency of the Au NPs on cotton swabs and has been widely used for active substrates to enhance the analyte Raman signal.<sup>23</sup> We systematically optimized the effects of NaCl concentration during the cotton



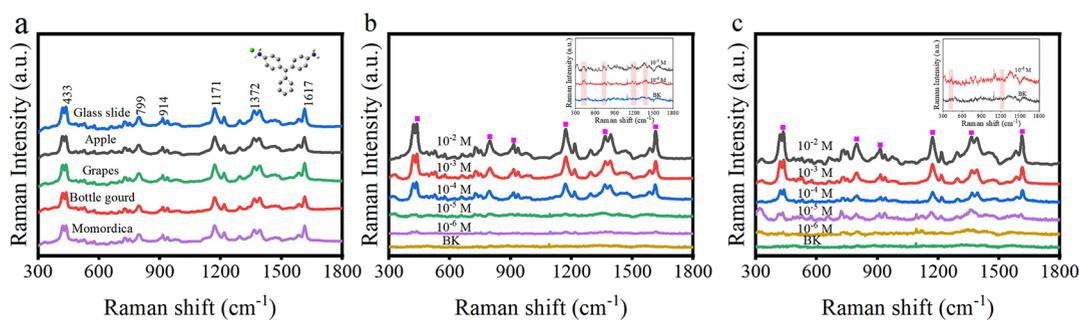
**Figure 5.** (a) SERS spectra for various concentrations of 4MPY obtained by CS-Au NPs. (b) Calibration curve intensity of 4MPY as a function of the concentration at  $1011\text{ cm}^{-1}$  (C in the  $x$  axis is an abbreviation for concentration). (c) SERS spectra of 4MPY at 12 randomly selected points on one wiper. (d) RSD evaluated using a  $1092\text{ cm}^{-1}$  specific peak intensity.

swab fabrication process to achieve the ultimate SERS advancement from CS-Au NPs. Figure 4a shows the Raman spectra of 4MPY ( $1 \times 10^{-5}\text{ M}$ ) evaluated from the small-head cotton swab substrate fabricated using different concentrations of NaCl (from 0 to 3.2 M). The Raman signal of 4MPY fluctuated as the concentration increased from 0 to 3.2 M, which is depicted in the inserted figure in Figure 4a. The cotton swab substrate displayed the lowest SERS signal intensity in the absence of NaCl in the growth medium. The intensity of the characteristic peak at  $1092\text{ cm}^{-1}$  increased as the NaCl concentration increased from 0 to 1.6 M. The increase in peak intensity is attributed to the aggregation of Au NPs in the presence of NaCl,<sup>27</sup> resulting in the formation of closely spaced gold nanoarrays on the surface of the fibers. Meanwhile, the attractive effect of NaCl on Au NPs enhanced the adhesion of Au NPs to the swab,<sup>23</sup> thus improving the modification of Au NPs and generating more hot spots. As the NaCl concentration continues to increase from 1.6 to 3.2 M, the bilayer structure of the Au NPs surface is significantly disrupted, leading to the formation of large gold nanoclusters<sup>23</sup> and thus reducing the SERS signal intensity. Therefore, we used the 1.6 M NaCl concentration for further research.

The SERS performance of a cotton swab coated with multiple Au layers (varying from 0 to 6) was further examined to determine the appropriate Au density in synthesizing the swab substrate for SERS analysis (Figure 4b). Following the first layer of Au NPs, a peak of 4MPY was detected at  $1092\text{ cm}^{-1}$  with an intensity of  $229\text{ cm}^{-1}\text{ a.u.}$  The peak intensity rises to 497 a.u. after the NP modification of the second layer. Next, further layering resulted in a decrease in the intensity

from 390 a.u. to 105 a.u. (inserted figure in Figure 4b). The Raman signal of the probe molecule (4MPY) did not exhibit an upward trend, indicating that the amount of Au NPs with two layers is optimal on the cotton swab. Therefore, we selected the optimized experimental conditions modifying two layers of Au NPs to prepare the SERS substrate.

**3.3. Sensitivity and Uniformity of the Optimized SERS Wiper.** In this study, high sensitivity or uniformity is our primary concern in developing SERS small-head cotton swabs. Figure 5a displays the SERS spectra of 4MPY at various concentrations ranging from  $10^{-8}$  to  $10^{-4}\text{ M}$  on the CS-Au NPs. The results show that the SERS signal intensity decreases as the concentration of 4MPY decreases. At  $10^{-8}\text{ M}$  concentration, the Raman signals are clear. This low LOD of 4MPY demonstrates excellent SERS sensitivity. The peak at  $1011\text{ cm}^{-1}$  is assigned as a quantitative peak to assess SERS sensitivity and activity of CS-Au NPs (Figure 5b). The intensity plot at  $1011\text{ cm}^{-1}$  demonstrated a simple linear increase with a logarithmic concentration of 4MPY from  $1 \times 10^{-4}$  to  $1 \times 10^{-8}\text{ M}$  ( $y = 135.9x + 1152.2$ ,  $R^2 = 0.9880$ ). In addition, the uniformity of SERS signals from small-head cotton swab substrates is another beneficial parameter in SERS measurements. We recorded the SERS spectra of 4MPY molecules with a concentration of  $1 \times 10^{-5}\text{ M}$  from 12 randomly selected points (Figure 5c) on the substrate. The results show that the Raman signal intensity of 4MPY in each spectrum was similar. In addition, the study quantitatively analyzed the point-to-point intensity variation of the characteristic peak at  $1092\text{ cm}^{-1}$  (Figure 5d). The calculated RSD was 10%, similar to previous research,<sup>26</sup> indicating good uniformity



**Figure 6.** (a) SERS spectra of MG on the surfaces of apple, grapes, bottle gourds, glass slides, and bitter gourds at a concentration of  $10^{-2}$  M/cm<sup>-2</sup>. The SERS spectra of MG with different concentrations acquired using fresh cotton swabs through swabbing extract on apples (b) and grapes (c).

of the prepared SERS substrates. This level of reliability can be attributed to the ease of fabrication and fundamental uniformity of the SERS cotton swabs. The sensitivity and evenness proved that the SERS cotton fabric is an ideal and promising SERS wiper.

**3.4. Detection of Pesticides on Different Surfaces.** An ideal SERS substrate must be capable of being used on various complex surfaces for target detection. A significant challenge for the practical use of the prepared flexible SERS substrates is to determine their ability to detect probe molecules on fruit surfaces. The CS-Au NPs substrate exhibits high sensitivity and uniformity in the detection of 4MPY, indicating that coated cotton fabrics have excellent potential for application in SERS detection on complex surfaces. To further evaluate the broad applicability of the fabricated substrate, MG, a widely and frequently used insecticide in agriculture,<sup>27</sup> was selected as the sample pesticide residue for rapid detection on a fruit surface using the wipe sampling method based on the abovementioned characteristics of CS-Au NPs. Hence, the surfaces of fruits and vegetables such as apples, grapes, bottle gourds, and bitter gourds were spiked with MG residues ( $10^{-2}$  M/cm<sup>-2</sup>) and detected using the Au NPs-CS substrate (Figure 6a). The Raman spectra exhibited peaks at 1171 and 1618 cm<sup>-1</sup>, attributed to the C–H bending and ring C–C stretching of MG molecules.<sup>28,29</sup> The results suggest that MG can be detected on different surfaces of apples, grapes, bottle gourds, glass slides, and bitter gourds. Figure 6b,c further summarized the analytical performances of CS-Au NPs on different SERS samples, and the results show that the LOD for MG is  $10^{-6}$  M, revealing that our SERS substrates are comparable to other SERS substrates reported in the literature (Table S1). In addition, the RSD at the Raman peak of 1171 cm<sup>-1</sup> obtained from the surfaces of grapes, apples, and bottle gourds was approximately below 15% (Table S2). This result illustrates the excellent ability of the CS-Au NPs for sensitive and conformal pesticide detection on regular or irregular matrices. Hence, this reliable CS-Au NP wiper has exceptional potential for the environmental monitoring and ultrasensitive detection of hazardous trace compounds in environmental science, agriculture, and bioscience.

## 4. CONCLUSIONS

This study used a simple and convenient method for synthesizing SERS-active substrates based on Au deposition onto a cotton fabric surface. We developed an optimal SERS cotton fabric substrate by carefully maintaining the thickness of the Au coating and adjusting the preparation conditions. The excellent performance of the SERS wiper was validated using

4MPY, which was detected at concentrations as low as  $10^{-8}$  M through SERS. The RSD of the peak intensity at 1092 cm<sup>-1</sup> was 10%, indicating excellent SERS wiper uniformity. Furthermore, the SERS cotton fabric can be used as a swab sample for the rapid detection of MG at low concentrations of  $10^{-6}$  M on the surface of apples, grapes, and bitter gourds. This scalable and repeatable method has significant potential in the agricultural, environmental, and bioscience industries for environment control and the ultrasensitive identification of contaminants in trace amounts.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c07690>.

(Table S1) Flexible SERS substrates for food safety detection; (Table S2) RSD (%) of different sample at 1171 cm<sup>-1</sup> ( $n = 5$ ) (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

Zhenli Sun – MOE Key Laboratory of Resources and Environmental System Optimization, College of Environmental Science and Engineering, North China Electric Power University, Beijing 102206, China; [orcid.org/0000-0002-4551-3374](https://orcid.org/0000-0002-4551-3374); Email: [sunzhenli1988@163.com](mailto:sunzhenli1988@163.com)

### Authors

Farzana Rafiq – MOE Key Laboratory of Resources and Environmental System Optimization, College of Environmental Science and Engineering, North China Electric Power University, Beijing 102206, China

Ning Wang – MOE Key Laboratory of Resources and Environmental System Optimization, College of Environmental Science and Engineering, North China Electric Power University, Beijing 102206, China

Keyou Li – MOE Key Laboratory of Resources and Environmental System Optimization, College of Environmental Science and Engineering, North China Electric Power University, Beijing 102206, China

Zijin Hong – MOE Key Laboratory of Resources and Environmental System Optimization, College of Environmental Science and Engineering, North China Electric Power University, Beijing 102206, China

Dandan Cao – MOE Key Laboratory of Resources and Environmental System Optimization, College of Environmental Science and Engineering, North China Electric Power University, Beijing 102206, China

Jingjing Du – State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

Complete contact information is available at:  
<https://pubs.acs.org/10.1021/acsomega.2c07690>

## Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was supported by National Natural Science Foundation of China (U21A20290, no. 21707077) and the Fundamental Research Funds for the Central Universities (no. 2020MS038).

## REFERENCES

- (1) Hong, J.; Kawashima, A.; Hamada, N. A simple fabrication of plasmonic surface-enhanced Raman scattering (SERS) substrate for pesticide analysis via the immobilization of gold nanoparticles on UF membrane. *Appl. Surf. Sci.* **2017**, *407*, 440–446.
- (2) Seiber, J. N.; Kleinschmidt, L. A. Contributions of pesticide residue chemistry to improving food and environmental safety: past and present accomplishments and future challenges. *J. Agric. Food Chem.* **2011**, *59*, 7536–7543.
- (3) Vickers, N. J. Animal communication: when i'm calling you, will you answer too? *Curr. Biol.* **2017**, *27*, R713–R715.
- (4) Panda, R.; Taylor, S. L.; Goodman, R. E. Development of a sandwich enzyme-linked immunosorbent assay (ELISA) for detection of buckwheat residues in food. *J. Food Sci.* **2010**, *75*, T110–T117.
- (5) Layne, J.; Lomas, S.; Misa, A. LC method development considerations for food contaminants analysis. *Am. Lab.* **2014**, *46*, 29–31.
- (6) Ferrer, C.; Martínez-Bueno, M. J.; Lozano, A.; Fernández-Alba, A. R. Pesticide residue analysis of fruit juices by LC–MS/MS direct injection. One year pilot survey. *Talanta* **2011**, *83*, 1552–1561.
- (7) Tahirbegi, I. B.; Ehgartner, J.; Sulzer, P.; Zieger, S.; Kasjanow, A.; Paradiso, M.; Strobl, M.; Bouwes, D.; Mayr, T. Fast pesticide detection inside microfluidic device with integrated optical pH, oxygen sensors and algal fluorescence. *Biosens. Bioelectron.* **2017**, *88*, 188–195.
- (8) Zhou, H.; Yang, D.; Ivleva, N. P.; Mircescu, N. E.; Niessner, R.; Haisch, C. SERS detection of bacteria in water by in situ coating with Ag nanoparticles. *Anal. Chem.* **2014**, *86*, 1525–1533.
- (9) Kurouski, D.; Van Duyne, R. P. In situ detection and identification of hair dyes using surface-enhanced Raman spectroscopy (SERS). *Anal. Chem.* **2015**, *87*, 2901–2906.
- (10) Lai, Y.-C.; Ho, H.-C.; Shih, B.-W.; Tsai, F.-Y.; Hsueh, C.-H. High performance and reusable SERS substrates using Ag/ZnO heterostructure on periodic silicon nanotube substrate. *Appl. Surf. Sci.* **2018**, *439*, 852–858.
- (11) Bassi, B.; Albini, B.; D'Agostino, A.; Dacarro, G.; Pallavicini, P.; Galinetto, P.; Taglietti, A. Robust, reproducible, recyclable SERS substrates: monolayers of gold nanostars grafted on glass and coated with a thin silica layer. *Nanotechnology* **2019**, *30*, No. 025302.
- (12) Shi, J.; You, T.; Gao, Y.; Liang, X.; Li, C.; Yin, P. Large-scale preparation of flexible and reusable surface-enhanced Raman scattering platform based on electrospinning AgNPs/PCL nanofiber membrane. *RSC Adv.* **2017**, *7*, 47373–47379.
- (13) Cui, H.; Li, S.; Deng, S.; Chen, H.; Wang, C. Flexible, transparent, and free-standing silicon nanowire SERS platform for in situ food inspection. *ACS sensors.* **2017**, *2*, 386–393.
- (14) Li, Y.; Wang, Y.; Fu, C.; Wu, Y.; Cao, H.; Shi, W.; Jung, Y. M. A simple enzyme-free SERS sensor for the rapid and sensitive detection of hydrogen peroxide in food. *Analyst* **2020**, *145*, 607–612.
- (15) Fang, X.; Song, Y.; Huang, Y.; Yang, G.; Han, C.; Li, H.; Qu, L. Two-dimensional MXene modified AgNRs as a surface-enhanced Raman scattering substrate for sensitive determination of polychlorinated biphenyls. *Analyst* **2020**, *145*, 7421–7428.
- (16) Bharati, M. S. S.; Soma, V. R.; Advanced Centre of Research in High Energy Materials (ACRHEM), University of Hyderabad, Telangana 500046, India. Flexible SERS substrates for hazardous materials detection: recent advances. *Opto-Electronic Advances.* **2021**, *4*, 210048–210048.
- (17) Kim, J.-H.; Twaddle, K. M.; Cermak, L. M.; Jang, W.; Yun, J.; Byun, H. Photothermal heating property of gold nanoparticle loaded substrates and their SERS response. *Colloids Surf, A* **2016**, *498*, 20–29.
- (18) Liu, S.; Guo, J.; Hinestroza, J.-P.; Kong, X.; Yu, Q. Fabrication of plasmonic absorbent cotton as a SERS substrate for adsorption and detection of harmful ingredients in food. *Microchem. J.* **2021**, *170*, No. 106662.
- (19) Betz, J. F.; Wei, W. Y.; Cheng, Y.; White, I. M.; Rubloff, G. W. Simple SERS substrates: powerful, portable, and full of potential. *Phys. Chem. Chem. Phys.* **2014**, *16*, 2224–2239.
- (20) Khan, G. A.; Demirtaş, Ö.; Demir, A. K.; Aytekin, Ö.; Bek, A.; Bhatti, A. S.; Ahmed, W. Fabrication of flexible, cost-effective, and scalable silver substrates for efficient surface enhanced Raman spectroscopy based trace detection. *Colloids Surf, A* **2021**, *619*, No. 126542.
- (21) Villa, J. E. L.; Quinones, N. R.; Fantinatti-Garborggini, F.; Poppi, R. J. Fast discrimination of bacteria using a filter paper-based SERS platform and PLS-DA with uncertainty estimation. *Anal. Bioanal. Chem.* **2019**, *411*, 705–713.
- (22) Cheng, D.; Bai, X.; He, M.; Wu, J.; Yang, H.; Ran, J.; Cai, G.; Wang, X. Polydopamine-assisted immobilization of Ag@ AuNPs on cotton fabrics for sensitive and responsive SERS detection. *Cellulose* **2019**, *26*, 4191–4204.
- (23) Kong, L.; Huang, M.; Chen, J.; Lin, M. Fabrication of sensitive silver-decorated cotton swabs for SERS quantitative detection of mixed pesticide residues in bitter gourds. *New J. Chem.* **2020**, *44*, 12779–12784.
- (24) Sun, Z.; Du, J.; Yan, L.; Chen, S.; Yang, Z.; Jing, C. Multifunctional Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Au Satellite Structured SERS Probe for Charge Selective Detection of Food Dyes. *ACS Appl. Mater. Interfaces* **2016**, *8*, 3056–3062.
- (25) Zhang, L.; Bai, Y.; Shang, Z.; Zhang, Y.; Mo, Y. Experimental and theoretical studies of Raman spectroscopy on 4-mercaptopyridine aqueous solution and 4-mercaptopyridine/Ag complex system. *J. Raman Spectrosc.* **2007**, *38*, 1106–1111.
- (26) Hu, H.; Song, W.; Ruan, W.; Wang, Y.; Wang, X.; Xu, W.; Zhao, B.; Ozaki, Y. Fabrication of one-dimensional ZnO/4-Mpy/Ag assemblies and their spectroscopic studies. *J. Colloid Interface Sci.* **2010**, *344*, 251–255.
- (27) Gong, L.; Wang, J.; Jiang, C.; Xiao, T.; Shen, K.; Lei, M.; Tang, Y. Study on Magnetic Porous Carbon Microspheres as a Novel Adsorbent for Malachite Green. *ChemistrySelect* **2021**, *6*, 3174–3182.
- (28) Chen, X.; Nguyen, T. H. D.; Gu, L.; Lin, M. Use of standing gold nanorods for detection of malachite green and crystal violet in fish by SERS. *J. Food Sci.* **2017**, *82*, 1640–1646.
- (29) Lu, S.; You, T.; Yang, N.; Gao, Y.; Yin, P. Flexible SERS substrate based on Ag nanodendrite-coated carbon fiber cloth: simultaneous detection for multiple pesticides in liquid droplet. *Anal. Bioanal. Chem.* **2020**, *412*, 1159–1167.