Adsorbent-SERS Technique for Determination of Plant VOCs from Live Cotton Plants and Dried Teas

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ABSTRACT: We developed a novel substrate for the collection of volatile organic compounds (VOCs) emitted from either living or dried plant material to be analyzed by surface-enhanced Raman spectroscopy (SERS). We demonstrated that this substrate can be utilized to differentiate emissions from blends of three teas, and to differentiate emissions from healthy cotton plants versus caterpillar-infested cotton plants. The substrate we developed can adsorb VOCs in static headspace sampling environments, and VOCs naturally evaporated from three plants. The substrate we developed can adsorb VOCs in static headspace sampling environments, and VOCs naturally evaporated from three plants. The performance of the SERS substrate, showing its ability to differentiate three VOCs and to detect quantitative differences according to collection times. In addition, volatile profiles from plant materials that were either qualitatively different among three teas or quantitatively different in abundance between healthy and infested cotton plants were confirmed by collections on Super-Q resin for dynamic headspace and solid-phase microextraction for static headspace sampling, respectively, followed by gas chromatography to mass spectrometry. Our results indicate that both qualitative and quantitative differences can also be detected by our SERS substrate although we find that the detection of quantitative differences could be improved.

1. INTRODUCTION

Volatile organic compounds (VOCs) are odorant compounds emitted from plant tissues. VOCs are responsible for the distinct aroma of certain dried plants, including the tea, Camellia sinensis. Therefore, VOCs can be used as an indicator of tea quality. In addition, the VOCs emitted from live plants play an important ecological role by attracting predators to the insect herbivores feeding on the plant. Cotton (Gossypium hirsutum) is an important crop for fiber production but its productivity has been significantly affected by major pests: the cotton aphid (Aphis gossypii), cotton bollworm (Helicoverpa armigera), beet armyworm (Spodoptera exigua), and stink bug (Nezara viridula). Herbivore-induced cotton volatiles can be utilized as a reliable indicator of insect infestation.

A popular contemporary method for analyzing VOCs is gas chromatography/mass spectrometry (GC/MS). This type of analysis first requires VOC collection; there are several collection methods, including (1) indirect extraction by solid-phase microextraction (SPME) fiber in static headspace, (2) purge and trap dynamic sampling involving drawing headspace air through a column packed with different adsorbent resins, or (3) direct extraction by distillation. Black, green, white, oolong, and pu-erh teas can be analyzed for quality by their VOC emissions. SPME is the most widely used technique for the analysis of the VOCs from tea samples, and the other two methods of dynamic headspace sampling and distillation are also utilized for some cases in which tea aroma needs to be collected. Cotton plant VOC emissions induced by insect herbivores are typically analyzed by dynamic headspace sampling with different adsorbents, and SPME has also been reported to collect the cotton VOC. Regardless of the collection method, GC/MS analysis is a very time-consuming process, requiring at least 30 min to complete just one analysis.

To overcome the lack of rapidity in GC/MS, electronic nose (e-nose) sensors have been developed. Dynamic sampling methods were coupled with an e-nose sensor for analyzing tea aroma. The FOX 4000 from a-MOS was applied to different tea infusions (green, black, and oolong) to evaluate its performance on the discrimination of grade level, and the EOS835 from Sacmi Imola s.c.a.r.l. was tested with green tea infusions to classify green tea samples with different storage periods. Additionally, the PEN from AIRSENSE Analytics...
was used to determine the differences in aroma profile between tea infusion and tea leaves\textsuperscript{28} and to distinguish different grades of green tea leaves.\textsuperscript{29} Likewise, a handheld e-nose system was developed for black tea aroma detection\textsuperscript{30} based on the optimized selection of four commercial tin-oxide-based MOS sensors. Also, a Pd-doped SnO\textsubscript{2} film was deposited on an interdigitated Au electrode and evaluated for its functionality in linalool tea aroma sensing.\textsuperscript{31}

For e-nose applications in cotton, Cyranose 320 has been used to analyze both stink-bug-damaged cotton bolls and the stink bug itself.\textsuperscript{32−34} In addition to using the commercial sensor, a low-cost portable e-nose sensor was designed by optimizing carbon black−polymer composites to detect the VOCs released from stink-bug-damaged cotton bolls.\textsuperscript{35} Although the e-nose has reasonable sensitivity for VOC detection with good rapidity, it requires additional training specific to the application before analysis and cannot always detect individual compounds.

Given the shortcomings of the two methods mentioned above, surface-enhanced Raman spectroscopy (SERS) is proposed as a measurement platform to analyze VOCs due to its specificity, rapidity, and sensitivity. Several different methods to fabricate SERS substrate have been proposed, and one of them was to use nanosphere lithography to precisely control the shape and gap size.\textsuperscript{36} In addition, nanoparticle array-based SERS substrate was developed as a cost-effective method,\textsuperscript{37} and a layer-by-layer technique was also involved to obtain a uniform nanoparticle film.\textsuperscript{38} Based on those fabricated substrates, many sensing applications have been reported to detect several target analytes,\textsuperscript{39} and, especially, different VOCs including acetone and benzene could be successfully detected by SERS techniques.\textsuperscript{40,41} However, there has not been determined whether the film can be effective for collecting VOCs released from live plants. Tenax-TA, 2,6-diphenyl-p-phenylene oxide porous polymer, has been widely applied to studies in which VOCs from botanicals and food need to be effectively collected as one of the adsorbents in dynamic sampling\textsuperscript{48,49} and it is easily dissolved in an organic solvent, enhancing its processability as a film from the dissolved polymer solution.\textsuperscript{50}

In this study, the unique SERS substrate, Tenax-TA deposited on a layer of Ag-nanosphere (AgNS), was developed and tested. The three objectives were to evaluate SERS spectra for multiplex detection of VOCs given by three different groups of sources: (1) authenticated VOC standards, (2) three different tea samples, and (3) cotton plants infested by beet armyworm caterpillars.

2. RESULTS AND DISCUSSION

2.1. Fabrication of ADS-SERS Substrate. A transmission electron microscopy (TEM) image (Figure 1a) shows that transferred AgNSs (TAgNSs) of about 100 nm in diameter
were formed from many Ag-nanocrystals less than 10 nm in diameter, and they had an adsorption peak at around 450 nm (Figure 1b), making them suitable as a SERS substrate.

A unique feature in our developed SERS substrate was the combination of the adsorbent polymer layer for VOC preconcentration with the SERS layer (Figure 1c). When the TAgNSs were used as the material for the first layer, the adsorbent layer formed very well on top due to hydrophobic interactions between the phenyl group of the adsorbent polymer and the hydrocarbon tail of the added surfactant of the TAgNS.

When the TAgNS-based substrate was compared with the WAgNS-based substrate, differences included polymer solution contact angle on the solid film and quality of adhesion. With WAgNS, the polymer solution contact angle was higher, and the adhesion quality was poor. However, with TAgNS, the adsorbent polymer layer was formed uniformly on a relatively larger area of the film, and great adhesion was observed, possibly due to the substantial work of adhesion from hydrophobic interactions.51,52 The differences are related to the interfacial phenomena between TAgNS solid film and adsorbent polymer in liquid and can also be explained by two well-known equations regarding interfacial energy53

\[
\cos \theta = -1 + \frac{2 \sqrt{\gamma_d \gamma_f}}{\gamma_f} + \frac{2 \sqrt{\gamma_p \gamma_l}}{\gamma_l}
\]

(1)

\[
W_a = 2 \left( \sqrt{\gamma_d \gamma_f} + \sqrt{\gamma_p \gamma_l} \right)
\]

(2)

where \( \theta \) is the contact angle (deg), \( W_a \) is the work of adhesion, and \( \gamma \) is the surface energy (J/m²). \( d \) represents the nonpolar dispersion part, \( p \) represents the polar part, \( s \) represents the AgNS solid film, and \( l \) represents the polymer in liquid.

From these equations, both contact angle and work of adhesion between two surfaces could be determined by nonpolar and polar molecular interactions. The polar term can be ignored in our case due to the strongly nonpolar property of the polymer. Therefore, only the nonpolar fluid properties were considered.

Figure 2. (a) Comparison of SERS spectra from the VOCs evaporated three standards according to the three different collection times, and (b) principal component analysis (PCA) plot based on SERS spectra.
compared according to the collection times in Figure 2a, and, the spectrum from each VOC adsorbed on the polymer was a peak.

VOCs adsorbed on the substrate was not enough to induce any of collection, which was exactly the same as the spectrum from our prepared substrate itself, meaning that the amount of the signature induced from three VOCs could not be found at 1 h achieved even at 3 h of collection time. However, any spectral notably, the multiplex detection of three VOCs could be larger values of cos θ (small contact angle) and Wc.

2.2. Determination of VOC Standards. The SERS spectrum from each VOC adsorbed on the polymer was compared according to the collection times in Figure 2a, and, notably, the multiplex detection of three VOCs could be achieved even at 3 h of collection time. However, any spectral signature induced from three VOCs could not be found at 1 h of collection, which was exactly the same as the spectrum from our prepared substrate itself, meaning that the amount of the VOCs adsorbed on the substrate was not enough to induce any peak.

The identified wavenumbers are summarized in Table 1, and the spectra from both linalool and methyl salicylate were more pronounced than those of cis-3-hexen-1-ol. The vapor from three droplets of VOC standards was generated by their vapor pressures at 25 °C and could be assumed to reach saturation at a certain time. Based on the ideal gas law, the maximum concentration for each volatile could be approximated (Supporting 1), and the actual concentration should be lower than the maximum until the vapor becomes saturated. This idea is supported by the fact that the peak intensity for the identified wavenumbers was more pronounced as the collection time increased and the maximum could be reached after overnight saturation. Quantitative differences between collection times were confirmed by PCA (Figure 2b), and all replicates from the 1 h collection were clearly separated from those from 3 h and overnight collection. In addition, the data for 3 h were closely located to those for overnight, showing that most of the VOCs could be saturated within 3 h and could be effectively preconcentrated on the ADS-SERS substrate.

The maximum concentration for methyl salicylate was the lowest among the three compounds (Table S1). However, many wavenumber peaks induced by methyl salicylate were observable in the SERS spectra. This fact could be explained in that Tenax-TA adsorbent was more effective for the preconcentration of the VOCs with lower polarity and higher boiling point. Although cis-3-hexen-1-ol or linalool was first attached on the adsorbent, it may have been displaced by methyl salicylate due to its phenyl group having higher affinity to the adsorbent. As shown in Figure 2a, methyl salicylate VOC evaporated from the standard for overnight had a very intense peak at the wavenumber of 812 cm−1, which corresponded to the approximated concentration, 45 ppm. Considering that the Raman intensity is proportional to the concentration, our substrate might be suitable for the detection of any VOC with a lower polarity like methyl salicylate at the sub-ppm level.

A few studies have developed a sensor to identify the VOCs used in our experiment but they focused on a single VOC rather than combined detection of multiple VOCs. For instance, a quartz crystal microbalance (QCM) sensor coated with an adsorbent layer such as poly(ethylene glycol) (PEG) or maltodextrin (MDEX) was proposed to identify the linalool or methyl salicylate from black tea. However, this type of sensor could not detect two VOCs simultaneously. In addition, the SERS technique, in which the AgNPs were modified with a specific linkage molecule, was specifically designed only for the detection of methyl salicylate. However, it was tested with methyl salicylate in the liquid phase, not the gas phase, and dispersion term needs to be considered, and TAgNS with a higher nonpolar portion than WAgNS can result in larger surface energy in the nonpolar term, which eventually causes larger values of cos θ (small contact angle) and Wc.

Table 1. List of the VOCs Affecting the SERS Spectra

| samples      | identified wavenumber (cm−1) | VOCs                                           |
|--------------|------------------------------|-----------------------------------------------|
| three standards | 1672                         | linalool (1672 cm−1)                           |
|              | 868                          | cis-3-hexen-1-ol (868, 971, 1020 cm−1)          |
|              | 972                          | methyl salicylate (810, 1033, 1135, 1158, 1252, 1585, 1615 cm−1) |
| black tea    | 1144                         | any compound with a secondary or tertiary alcohol in 
|              | 1268                         | any compound with an aromatic component with ortho-disubstituted in |
|              | 1072                         | β-pinene (852 cm−1)                            |
|              | 1452                         | p-cymene (818, 1618 cm−1)                       |
|              | 1496                         | butyric acid (863 cm−1)                        |
| Earl Grey    | 852                          | α-pinene (668, 840 cm−1)                        |
|              | 816                          | acetoic (768 cm−1)                             |
|              | 856                          | phellandrene (1585 cm−1)                       |
| rooibos      | 768                          | octanal (1504 cm−1)                           |
|              | 828                          | phellandrene (1585 cm−1)                       |
| cotton       | 672                          | (Z)-3-hexenyl acetate, (E)-2-hexenyl acetate (1742 cm−1) |
|              | 1584                         | (Z)-3-hexenyl acetate, (E)-2-hexenyl acetate (1742 cm−1) |
|              | 1620                         | (Z)-3-hexenyl acetate, (E)-2-hexenyl acetate (1742 cm−1) |

“Possible molecular group that can affect these wavenumber regions.
might not be effective for molecules other than methyl salicylate.

2.3. Determination of Tea Aroma. Major compounds identified through GC/MS analysis of tea were qualitatively different for each sample (Table 2). Easily noticeable is a higher proportion of phthalate ester in the black tea sample, a compound known as a carcinogenic material that can directly affect human health. Other reports have detected phthalate ester in tea samples contaminated by environmental sources or plastic,8,58 so our finding could be a result of contamination in the black tea samples. Many different terpenes were detected from the Earl Grey tea samples; both linalool and linalool oxides are important terpene derivatives that can contribute to tea flavor and aroma.12 Finally, several VOCs including acetoin and butyric acid were identified from rooibos tea samples, and they also have been previously reported as volatile components from rooibos tea.60,61

Raman spectra of the VOCs identified by GC/MS were investigated using commercial libraries, and possible matching with the SERS spectra from each tea (Figure 3) was summarized (Table 1). From the SERS spectra of black tea samples, several intense peaks were observed at three wavenumber regions of 1072, 1452, and 1496 cm$^{-1}$, and three phthalate esters from black tea may be the main components affecting those peaks. As commercial libraries of any phthalate ester were not available, an additional function in KnowItAll software aided the selection of molecular groups based on the peak locations (Figure S1). An aromatic component with ortho-disubstituted was suggested as a possible candidate (Figure S1a); its Raman peaks have been identified at regions similar to those from black tea and are associated with several vibrational modes of aromatic ring bending–stretching and C–H in-plane H bending. The general structure of phthalate is that of an ortho-disubstituted aromatic compound, so several phthalate esters from black tea may strongly affect these three wavenumbers. A previous article regarding the detection of the phthalate ester in plastics by Raman showed that two characteristic peaks were found at 1450 and 1040 cm$^{-1}$, which could support our result.63 The other two intense peaks were also observed at the wavenumbers of 1144 and 1268 cm$^{-1}$, and any secondary or tertiary alcohol that can result in two wavenumber regions by C–O–H deformation and C–C–O stretching is suggested in Figure S1b. Therefore, two alcohols in Table 2, 2-hydroxyisobutyric acid for tertiary and 3-penten-2-ol for secondary, might be also possible VOCs affecting these two wavenumbers. A strong and broad peak was found in the SERS spectra from Earl Grey tea at the 1620 cm$^{-1}$ wavenumber, and it is associated with the mode of bending–stretching by the aromatic ring of p-cymene.64 Two small peaks between 900 and 800 cm$^{-1}$ corresponded to the spectra from p-cymene and $\beta$-pinene. In the case of rooibos tea, no significant peak was observed relative to the other two teas, but two small peaks were found at 768 cm$^{-1}$ corresponding to acetoin and 856 cm$^{-1}$ related to butyric acid.

Two multivariate analyses with the identified wavenumbers showed great discrimination among the three tea samples (Figure 4). From the data for a 3 h collection, one replicate for black tea did not separate well from rooibos but all of the data points were clearly separated for each tea after overnight collection due to increased intensities at the identified wavenumbers. In addition to PCA, the classification accuracy for the linear discriminant analysis (LDA) model is summarized in Table 3, averaged from 10 replicates. The overnight experiment provided nearly perfect classification (100% accuracy), while the 3 h experiment resulted in an 87% accuracy.

2.4. Determination of Caterpillar-Induced Cotton VOCs. The SPME collections from healthy and infested cotton plants revealed qualitative and quantitative differences in VOC emissions (Figure 5). (E)-2-Hexenal, (E)-2-hexenyl acetate, caryophyllene, humulene, and isoamyl acetate were detected in emissions from caterpillar-infested plants but not from healthy plants. The most abundant VOC was $\alpha$-pinene in both healthy and infested plants. The t-tests ($\alpha = 0.05$) revealed that all compounds, shared between healthy and infested samples, (Z)-3-hexenyl acetate and the monoterpenes, were significantly more abundant from infested plants, except for sabinene ($\alpha$-pinene: $P = 0.004$; $\beta$-pinene: $P = 0.006$; limonene: $P = 0.050$; ocimene: $P = 0.027$; phellandrene: $P = 0.031$; sabinene: $P = 0.128$; and (Z)-3-hexenyl acetate: $P = 0.027$).

Some wavenumber regions (Figure 6a) that could differentiate between healthy and infested cotton plants were identified and most of them were located between 1750 and 1550 cm$^{-1}$. First, 1620 cm$^{-1}$ was clearly identified only in infested cotton but the specific VOC responsible was not determined. A possible VOC affecting the peak at that wavenumber is caryophyllene, with a characteristic peak at 1630 cm$^{-1}$.65 The peak shift of more than 10 cm$^{-1}$ can be explained by the geometric orientation of the adsorbed molecule to the surface of the SERS substrate.66 Second, two other peaks were also shown at 1744 and 1584 cm$^{-1}$ only in the infested case and these fairly closely correspond to the main characteristic peak of (Z)-3-hexenyl acetate or (E)-2-hexenyl acetate and phellandrene, respectively. Third, a peak at 1604 cm$^{-1}$ was detected in healthy and infested cotton, so a shared compound could be responsible, possibly ocimene, with a weak band at that wavenumber. Finally, two other peaks were also observed at 828 and 672 cm$^{-1}$ only in the infested case, and they may be associated with the vibrational property caused by $\alpha$-pinene. Although the peak intensities for all of the identified VOCs that could differentiate between the two treatments were not high, the PCA plot in Figure 6b showed clear discrimination such that all biological replicates from

| tea samples | VOCs                             | percentage (%) |
|------------|----------------------------------|----------------|
Figure 3. (a) Comparison of SERS spectra from three different tea aromas for a 3 h collection, and (b) comparison of SERS spectra from three different tea aromas for overnight collection. BT: black tea, EG: Earl Grey, RB: rooibos.

Figure 4. (a) PCA plot based on SERS spectra of tea aromas for a 3 h collection, and (b) PCA plot based on SERS spectra of tea aromas for overnight collection. BT: black tea, EG: Earl Grey, RB: rooibos.
healthy cotton were located along the negative component 1 axis, but those from infested cotton were located along the positive axis. In addition, the PCA in Figure 6c also showed reasonable discrimination such that most of the technical replicates from the infested cotton were likely to be positioned along the positive axis, but those from the healthy were likely to be positioned along the negative axis.

3. CONCLUSIONS

A simple and cost-effective SERS substrate was developed to determine the VOCs given off by dried teas and live cotton plants. Three tests were successfully used to demonstrate this SERS substrate’s ability for simultaneous qualitative detection of multiple VOCs. We also found the potential for quantification because there was a large intensity difference associated with VOC collection times. Based on the fact that our substrate had higher sensitivity to some VOCs including methyl salicylate, pthalate ester, and p-cymene, the substrate could be considered as a useful sensing platform for detecting any VOCs having an aromatic group. To the best of our knowledge, our study is the first to report direct SERS sensing by dried teas and live cotton—the TAgNS solution was first drop-cast on the cleaned quartz substrate and fully dried. Thereafter, 5 μL of the adsorbent solution was also deposited on the spot where the TAgNSs were concentrated by centrifugation and redispersion with dichloromethane. To fabricate the ADS-SERS substrate, Tenax-TA polymer was dissolved in dichloromethane (10 mg/mL) for the adsorbent solution, and a 5 μL volume of the TAgNS solution was first drop-cast on the cleaned quartz substrate and fully dried. Then, the mixture was vortexed for 1 min, and the TAgNSs were concentrated by centrifugation and redispersion with dichloromethane. The phase transfer of the AgNS was performed with some modifications to our previous methodology, and the fabrication of ADS-SERS substrate is introduced here. To fabricate AgNS, exactly 0.5 g of AgNO3, 10 mL of deionized (DI) water, 0.8 g of sodium oleate, 1 mL of oleic acid, and 5 mL of ethanol were mixed together in a glass vial under agitation. The vial was sealed and heated overnight at 150 °C. A layer of Ag-nanocrystal formed at the bottom of the vial, 80 mg of which was dissolved in 20 mL of cyclohexane. Exactly 560 mg of sodium dodecyl sulfate was dissolved in 100 mL of DI water, and the two solutions were mixed together. AgNSs were finally prepared by sonicating the mixture for 1 h and heating it at 70 °C until the cyclohexane was almost completely evaporated. For the phase transfer of the AgNS, tetracyclammonium bromide cationic surfactant solution was prepared by dissolving it in 0.14 M dichloromethane, and 100 μL of the surfactant solution was mixed with 100 μL of the AgNS solution. Then, the mixture was vortexed for 1 min, and the TAgNSs were concentrated by centrifugation and redispersion with dichloromethane. The insects, S. exigua larvae, were purchased as eggs from Benzon Research and reared on an artificial diet of Helicoverpa zea purchased from Southland Products Incorporated and supplemented with a 7 mL of raw linseed oil per batch of diet. Insect-rearing conditions were light/dark for 14:10 h at 28:25 °C. Insects were reared until the third instar on their artificial diet and then transferred into glass Petri dishes with excised leaves of conventional (nongenetically modified) cotton. They were allowed to feed on the conventional cotton leaves for at least 24 h before being used in experiments. This acclimated the larvae to feeding on plant material so that they would readily accept the leaves as food during the experiments.

4. EXPERIMENTAL SECTION

4.1. Material Description. VOC standards including linalool, cis-3-hexen-1-ol, and methyl salicylate and Tenax-TA (60/80 mesh) adsorbent from Sigma-Aldrich were used. Three different tea samples including black tea, Earl Grey, and rooibos tea were commercially available products, and they were directly used as experimental materials without pretreatment.

4.2. ADS-SERS Substrate. The fabrication of ADS-SERS substrate was composed of three steps: (1) the fabrication of WAgNS, (2) phase transfer of the AgNS to organic solvent, and (3) adsorbent polymer deposition on the TAgNS film. The phase transfer of the AgNS was performed with some modifications to our previous methodology, and the fabrication of ADS-SERS substrate is introduced here. To fabricate AgNSs, exactly 0.5 g of AgNO3, 10 mL of deionized (DI) water, 0.8 g of sodium oleate, 1 mL of oleic acid, and 5 mL of ethanol were mixed together in a glass vial under agitation. The vial was sealed and heated overnight at 150 °C. A layer of Ag-nanocrystal formed at the bottom of the vial, 80 mg of which was dissolved in 20 mL of cyclohexane. Exactly 560 mg of sodium dodecyl sulfate was dissolved in 100 mL of DI water, and the two solutions were mixed together. AgNSs were finally prepared by sonicating the mixture for 1 h and heating it at 70 °C until the cyclohexane was almost completely evaporated. For the phase transfer of the AgNS, tetracyclammonium bromide cationic surfactant solution was prepared by dissolving it in 0.14 M dichloromethane, and 100 μL of the surfactant solution was mixed with 100 μL of the AgNS solution. Then, the mixture was vortexed for 1 min, and the TAgNSs were concentrated by centrifugation and redispersion with dichloromethane.

### Table 3. LDA Model Validation by k-Fold Cross-Validation (k = 6)

| Method | LDA classification accuracy (%) | Average (%) |
|--------|---------------------------------|-------------|
| black tea vs Earl Grey vs rooibos | 89 89 89 83 89 83 89 83 89 83 89 87 | 100 100 100 100 100 100 100 100 100 100 100 100 |

Figure 5. Comparison of the identified VOC abundances by SPME–GC/MS between healthy and infested cotton.
4.4. VOC Collection by ADS-SERS Substrate. The prepared ADS-SERS substrate was finally used for the preconcentration of VOCs from various sources in the static headspace sampling setup (Scheme 1), and the size of the chamber varied depending on what kinds of samples were prepared as VOC sources. The VOC collection started immediately right after the samples were placed in the chamber.

4.4.1. VOC Standards. Three 5 μL droplets of linalool, cis-3-hexen-1-ol, and methyl salicylate were dispensed in a 120 mL jar. The ADS-SERS substrate was situated against the wall of the jar facing the three droplets (Scheme 1a). Three trials were performed with collection times of 1 h, 3 h, and overnight. As a control, one substrate was kept inside an empty jar. All trials were replicated 6 times.

4.4.2. Tea Aroma. Exactly 10 g of each tea sample was placed inside a 120 mL glass jar for 3 h and overnight, and the ADS-SERS substrate was also located against the wall of the glass facing the tea sample (Scheme 1b). These experiments were replicated 6 times.

4.4.3. Cotton VOCs. A single plant was placed inside a chamber. We fashioned a standout of a metal wire, which hung off the side of the pot and held the ADS-SERS substrate (Scheme 1c). The substrate was held with the narrow edge vertical so that droppings from the caterpillars would not land on the substrate and contaminate the sample. Experimental conditions were the same as rearing conditions other than the plants inside the glass chambers with static headspace for the experiments. Using soft forceps, we placed five total third- and fourth-instar larvae in one experimental chamber (the other chamber was herbivore-free), and both chambers were then sealed. The experiments took place over 48 h with the plants being enclosed and removed midday. This experiment was replicated 3 times. The size of the chamber was much larger than the previous glass jar, so VOC collection efficiency from the chamber might not be better than that from the small-sized jar. For this reason, four technical replicates were performed per one biological replicate to improve the collection efficiency.

4.5. VOC Collection by Commercial Adsorbent. 4.5.1. Dynamic Sampling for Tea Aroma. Exactly 10 g of each tea sample was placed inside a 120 mL glass jar capped with a Teflon lid. Each glass jar was connected to two glass columns (178 mm length × 6 mm O.D.; Supelco, Bellafonte, PA) filled with a 5 cm bed of Hayesep Q resin (80/100 mesh; Hayes Separations, Inc., Bandera, TX): one column was for...
dynamic VOC collection and the other was for cleaning the air entering the jar. The VOC dynamic collection was performed with a diaphragm pump (Thomas Scientific,) at a rate of 1 L/min for 1 h.

4.5.2. Static Sampling for Cotton VOCs. Poly(dimethylsiloxane) (PDMS)/divinylbenzene (DVB)/Carbowax 50/30 μm coating SPME fibers by Supelco (Millipore-Sigma, St. Louis, MO) were exposed to the static headspace of the chamber during the final 30 min of the experiment (Scheme 1c).

4.6. Equipment Used. 4.6.1. Adsorbent-GC/MS. The VOCs collected dynamically were eluted from the resin with 500 μL dichloromethane and analyzed by a Shimadzu GCMS-QP2010 Ultra (Shimadzu Scientific Instruments (Oceania) Pty Ltd., Henderson, New Zealand). We used the Zebron ZB-WAXplus capillary GC column from Phenomenex, which is 30 m in length with an internal diameter of 0.25 mm and a film thickness of 0.25 μm. The temperature at the injection port with a flow rate of 1.5 mL/min was 250°C, and a 1 μL eluate was injected with a split ratio of 1. The oven temperature program was initiated at 40°C and held for 3 min, then was increased to 240°C at 5°C/min and held for 3 min, and then increased to 250°C at 40°C/min to purge the column. Manual injections with the SPME fibers were performed with a hollow-bore splitless injection port and a desorption time of 2 min at 230°C with the total injection port airflow at 1.5 mL/min. The oven temperature program was initiated at 60°C and held for 2 min, increased to 180°C at 4°C/min, then increased to 250°C at 50°C/min, and held for 4 min to purge the column. Identification of VOCs was based on the comparison of retention times to authentic standards and mass spectra stored in the National Institute of Standards and Technology (NIST) and Wiley Registry (10th edition).

4.6.2. Raman Spectroscopy. All ADS-SERS substrates were analyzed by Raman spectroscopy (RamanStation 400F, PerkinElmer, Beaconsfield, Buckinghamshire, U.K.) with a 256 x 1024 pixel CCD detector and a 785 nm near-infrared laser with 175 mW power. They were placed on the stage of the Raman spectrometer, and a spectrum was collected with a 2 s exposure time at a spectral resolution of 4 cm⁻¹ in the Raman shift range of 200–2000 cm⁻¹. The spectra were finally compared to the VOCs identified by GC/MS using commercial Raman libraries (KnowItAll Informatics System 2018, Bio-Rad Laboratories, Inc.), and all relevant Raman libraries are included in the Supporting Information. For the VOC that was not identified from either any reference or the commercial libraries, Raman spectrum from the VOC was generated from the corresponding standard and included in the Supporting Information (S3).

4.6.3. Transmission Electron Microscope (TEM). Approximately 3 μL of the TAgNSs was sampled to the grid and perfectly dried. The dried sample on the grid was analyzed in a JEOL 1200 EX transmission electron microscope (TEM) operated at an acceleration voltage of 100 kV, and morphological images were captured with a 3k slow-scan CCD camera (model 1SC, SIA).

4.6.4. UV/Vis Spectroscopy. A 100 μL volume of the TAgNS was sampled inside a quartz cuvette, and UV/vis–near-infrared (NIR) spectra were collected with a Hitachi U-4100 spectrophotometer.

4.7. Statistical Analysis. 4.7.1. Descriptive Statistics. For GC/MS data generated with SPME, the peak area for each
identified VOC was calculated with the Shimadzu GCMSolution (version 2.7) package software. These values were fourth-root-transformed, and VOCs that were shared in the healthy and infested were individually compared using one-sided t-tests under the hypothesis that abundances are greater from infested plants.

For Raman data, all spectral information was exported from the Spectrum (v6.3) software, and the data were preprocessed by baseline correction and normalization with the bioinformatics toolbox of MATLAB. The processed data were finally averaged out from all replicated data.

4.7.2. Multivariate Analysis. All wavenumbers from Raman data were considered as variables, and optimal sets of wavenumber variables were selected from all variables based on the wavenumbers corresponding to identified peaks associated with the VOCs produced from different sources.

To identify three VOCs according to the collection time, unique sets of variables determined based on the wavenumber peaks induced by three VOCs were shown, and principal component analysis (PCA) was performed in JMP 13 Pro (SAS Institute Inc.) with the selected variables. Finally, the first two principal components were plotted to determine whether the replicates could be clustered according to the collection time.

To determine tea variety, specific wavenumbers were chosen as a final variable set from the identified peaks induced by the aromas of three teas. PCA was also applied to the Raman tea data with this variable set. The first two principal components were again plotted to determine how the replicates from the three tea samples could be clustered. In addition, linear discriminant analysis (LDA) was applied in R software to the same data set to create an LDA classification model that can predict which tea variety each data point belongs to. Model accuracy was evaluated by 6-fold cross-validation with custom R code that divided all of the data into four groups, and each group included three data points randomly selected from each tea sample.

To detect caterpillar infestation on cotton, variable optimization was performed by selecting wavenumbers associated with cotton VOCs, and PCA was run with the selected data set. The first two principal components were again plotted to determine whether the replicates from the infested and noninfested cotton samples could be clustered.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03500.

Gas concentration approximation for three VOCs; possible molecular groups: aromatic component with ortho-disubstituted and any secondary or tertiary alcohol; Raman spectra for standards relevant to Earl Grey VOC, rooibos VOC, and cotton VOC (PDF)

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Notes

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