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Article

Hydrophobic Plasmonic Filter Paper SERS Substrate for Monitoring Harmful Ingredients from Food Sample

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Abstract

A flexible paper base SERS substrate with hydrophobic surface was fabricated through a simple route. The Ag nanoparticle was modified on filter paper through in situ growth method. After optimizing the condition during the growth and surface modification process, the hydrophobic filter paper-Ag was prepared via soaking in 10^{-8} g/ml of 1-Dodecanethiol with 12 h growth time. The flexible SERS substrate exhibit excellent hydrophobic properties, the contact angle of water could achieve 130.2° . When the solution of analyte was dropped onto the SERS substrate, the diffusion effect was limited. After evaporation, the target analyte was concentrated within a fixed area. The hydrophobic SERS substrate could simultaneously improve the SERS signal and fluorescence of the analyte. The paper base SERS substrate with hydrophobic surface was used for detecting thiram from edible oil, and the sensitivity was down to 10^{-7} M. We proposed a flexible, economical and green hydrophobic SERS substrate for the detection of harmful ingredient from hydrophobic phase.

Keywords: hydrophobic; filter paper; SERS; harmful ingredients; food

1. Introduction

Surface enhanced Raman scattering (SERS) spectroscopy is an important analytical tool [1,2]. SERS method has shown several advantages such as high sensitivity and unique molecular specificity, that was developed in recent decades as the emerged of nanotechnology SERS could provide ultrasensitive information of target down to the single-molecule level [3–5]. Thus, SERS was widely applied in analytical chemistry, food safety and biochemical analysis. Currently, there are two widely accepted theories regarding the SERS enhancement mechanism: electromagnetic enhancement (EM) and chemical enhancement (CE) [6,7]. Compared with the chemical enhancement mechanism, the strong electromagnetic field generated near metal nanoparticle (NP) is the fundamental reason for the generation of SERS [8,9]. Therefore, SERS performance mainly relies on enhanced substrates, that was prepared based on metallic nanomaterials. The rigid SERS substrate such as glass, silicon and quartz were usually used as support in SERS substrate, that lacked flexibility in some practical applications, which poses significant limitations for analysis and detection of irregular objects [10].

Flexible SERS substrates offer benefits such as flexibility, high activity, and biodegradability, that has attracted great attention. Filter paper was widely used to construct SERS substrate due to its low cost, simplicity, and ease of production [11–14]. The filter paper was rich with hydroxyl groups because that was composed of cellulose fibers, and special molecule could be easily functionalized

on the surface of filter paper. The wrinkle on filter paper enables the formation of "hot spot" for SERS as metallic NPs deposited on surface cellulose fiber [15–17]. At present, there are many methods for preparing paper-based SERS substrates by depositing filter paper with metallic NPs, such as in situ synthesis [18,19], inkjet printing [20,21] and self assembly [22,23]. The SERS substrates prepared by these methods exhibit high repeatability and sensitivity. However, the liquid sample was rapidly diffuse when using paper base substrate as the hydrophilicity and rich porosity of paper that would reduce the collection efficiency of the samples at a certain position and further decrease the intensity of Raman spectrum.

To address the issue of excessive hydrophilicity of filter paper SERS substrates, we introduced the concept of hydrophobicity. Recently, there have been many researches on hydrophobic SERS substrate, that have shown unique advantage in detecting low concentrations of target analyte [24–27]. The significant advantage of hydrophobic SERS substrates is that could reduce the contact area between aqueous droplet and the surface of SERS substrates. Therefore, the number of aqueous target analyte was significantly concentrated on the hydrophobic substrate during the evaporateing process. Li et al. have loaded silver nanoparticles onto a cellulose nanocrystalline skeleton by in situ growth method to prepare cellulose nanocrystalline silver (CNC-Ag) composite, which further coated on the surface of filter paper to form a flexible substrate. The dodecyl mercaptan was employed for treating the surface with hydrophobic feature, and the contact angle could reach to 105 °. The hydrophobic filter paper substrate was successfully used to detect phenylethanolamine A and metronidazole [28]. Nat rcia et al. have fabricated SERS substrate by changing the relative amount of polymer/metal colloidal nanoparticles, the number of printing layers, and the hydrophobicity ,in which the contact angle could achieve to 146 °. In SERS detection of thiram in mineral water and apple juice, the limit of detection could down to 0.024 ppm [29].

In this study, we prepared a simple, inexpensive, and easy-to-operate flexible SERS substrate with hydrophobic feature as shown in Figure 1. Firstly, the silver NPs were densely deposited on the surface of filter paper by seed-mediated in situ growth method. Then, the solution of dodecyl mercaptan were grafted onto the surface of silver NPs. The concentration and soaking time were optimized for the flexible SERS substrate with hydrophobic surface. The hydrophobic feature could effectively prevent random diffusion of the target analyte solution, which not only improve the intensity of Raman spectra but also enhance the fluorescence effect. The flexible SERS substrate with hydrophobic surface was successfully used for detecting melamine and thiram from water. Furthermore, the hydrophobic SERS substrate proposed at here shown excellent performance in detecting target from oil phase compare with the hydrophilic SERS substrate.

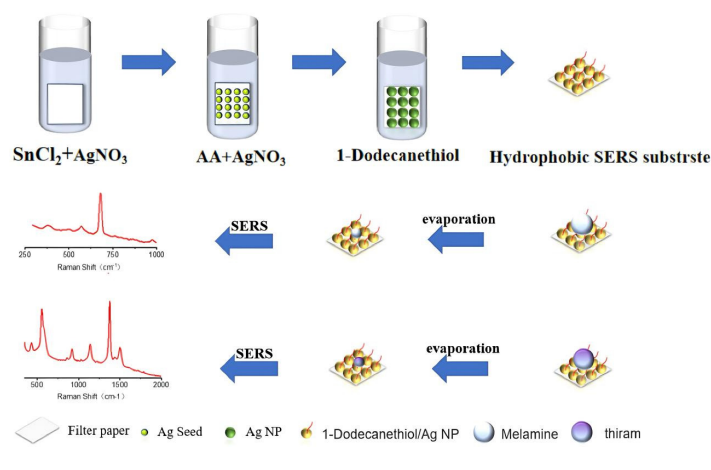


Figure 1. Fabricating and applying the hydrophobic SERS sensor.

2. Experiment

2.1. Chemicals

Ascorbic acid ($C_6H_8O_6$, AA) and hydrochloric acid (HCl) were supplied by Aladdin (Shanghai, China). Silver nitrate ($AgNO_3$), Rhodamine6G (R6G) and thiram were purchased from Innochem (Beijing, China). Melamine was purchased from the Shanghai Reagent Company. 1-Dodecanethiol was obtained from Alfa Aesar (Shanghai, China). Edible oil was purchased from the local supermarkets.

2.2. Preparation of SERS Substrate

Silver NPs (Ag NPs) were densely deposited onto the surface of filter paper through in situ growth technology. Briefly, soaked filter paper with aqueous solution of $SnCl_2/HCl$ (20 mM: 20 mM) for 30 S. After that, the Ag seed was produced in $AgNO_3$ (20 mM). The Ag NPs with bigger size were obtained by soaking filter paper-Ag seed in mixture of AA and $AgNO_3$. Finally, the filter paper was isolated from the growth media and washed.

2.3. Hydrophobic Treatment

The prepared filter paper SERS substrates were soaked in different concentrations of ethanol solution of 1-Dodecanethiol (10^{-4} , 10^{-6} , 10^{-8} , 10^{-10} , 10^{-12} , 10^{-14} , 10^{-16} , 10^{-18} g/ml) for 12 hours, then washed with ethanol for several times and dried at room temperature to obtain filter paper SERS substrates with hydrophobic feature.

2.4. Sample Preparation and SERS Testing

In the experimental detection, 3 microliters of target analyte solution were dropped onto the hydrophobic surface of filter SERS substrate, the Raman spectra was measured by a portable Raman spectrometer (BWS465, B&W Tek, USA) with laser at 785 nm.

2.5. Characterization and Analysis

The UV-vis spectra of the composites were measured by Agilent UV-Vis-NIR spectrometer (Agilent USA). The surface morphology of sample were collected from SU8010 scanning electron microscope (SEM) (Hitachi, Japan). Thermo gravimetric analysis (TGA) was developed by Perkin-Elmer (PE USA). ATR-FTIR was measured on Nicolet iS50 infrared instrument. The water contact angle (WCA) test of hydrophobic surface was conducted on DSA100 instrument (KRÜSS, Germany).

3. Results and Discussion

3.1. Morphology Characterization

Filter paper SERS substrate was prepared using in situ growth technology. The SEM images of the filter paper are shown in Figure 2a,b, in which the cellulose fiber was observed. When the filter paper soaked in aqueous solution of $SnCl_2$, the Sn^{2+} was adsorbed onto the surface of the cellulose fiber through its affinity with hydroxyl groups. The cellulose ribbon on the surface of filter paper provide the area for the uniform distribution of Ag NPs. The reduction potential value of Sn^{4+}/Sn^{2+} was 0.151 V and the value is 0.80 V for Ag^+/Ag^0 . Thus, the Ag^+ was reduced to Ag and formed nanoseed as encountered with Sn^{2+} . When immersed the filter paper with Ag seed into growth media, the Ag seed was growth to Ag NP with bigger size. SEM image of the Ag NPs distributed on the surface of filter is shown in Figure 2c, in which the size of Ag NPs is distributed within 60-80 nm. In order to obtain hydrophobic surface, the 1-Dodecanethiol was used to modify the surface of Ag NPs through chemical bond between sulfhydryl and Ag. After modified with 1-Dodecanethiol, the

morphological image of filter paper substrate is shown in Figure 2d, there is no obvious change compare with the substrate before modification.

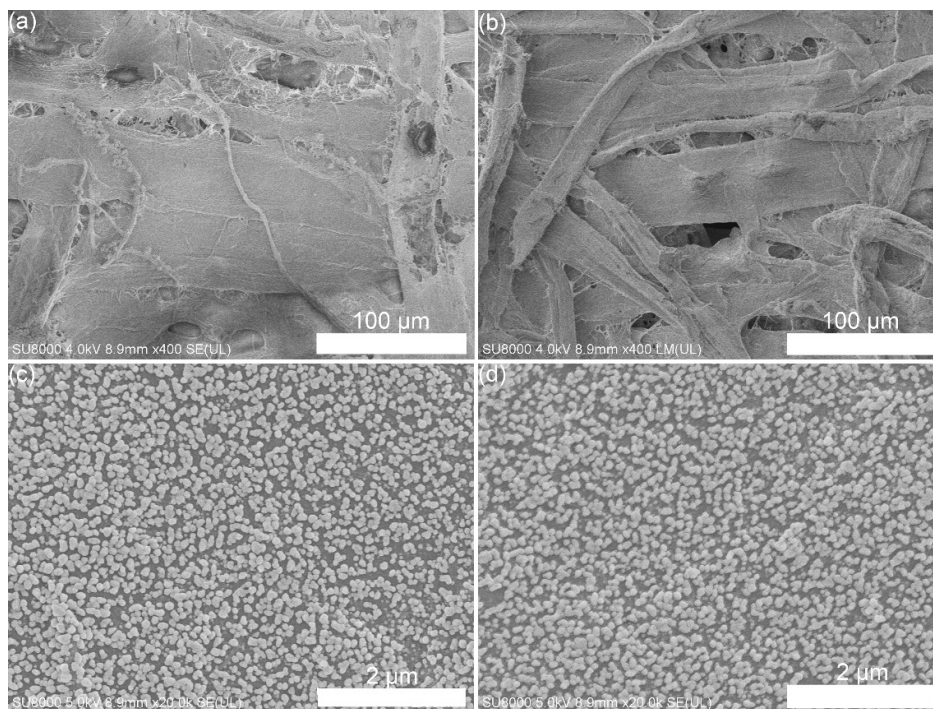


Figure 2. SEM image of filter paper (a,b) and SERS substrate before (c) and after modification with 1-Dodecanethiol (d).

3.2. SERS Performance

The filter paper SERS substrate were immersed in ethanol solution of 1-dodecanethiol for different reaction times (6, 8, 10, 12, 14, and 16 hours). The enhancement effect of SERS substrates was evaluated by using R6G as Raman probe molecule. 3 μ L R6G was dropped onto the surface of a hydrophobic filter paper-Ag. After drying at air condition the Raman spectra was collected and presented in Figure S1a. Several obvious Raman peaks were observed at 1308 cm^{-1} , 1360 cm^{-1} and 1508 cm^{-1} , these peaks were assigned to the stretching vibration mode of C-O-C and aromatic C-C groups of R6G [30]. At the initial stage, the 6 h soaking time used in the system, the weak Raman spectra of R6G was obtained, because the Ag NPs were not fully modified by 1-Dodecanethiol. The analyte would diffuse on the surface of SERS substrate with low hydrophobicity, that resulting in a low Raman signal. The Raman signal of R6G were increased as prolong the soaking time, and the soaking time of 12 h provides the highest SERS enhancement effect. From the comparison of Raman intensity of R6G of band at 1360 cm^{-1} from different filter paper SERS substrate (Figure S1b), the substrate soaked in 1-Dodecanethiol for 12 h was observed to shown the best SERS enhancement. The further increasing of soaking time bring the decrease of the Raman signal, that maybe due to the multilayer formed as long soaking time used. The distance between analyte and Ag NPs was increased.

3.3. Hydrophobic Property

As a result of 1-Dodecanethiol is insoluble in water, the dense 1-dodecanethiol coating on the surface of Ag NPs brings a decrease in the affinity between SERS substrate with water molecules and thereby increasing hydrophobicity in comparison to filter paper SERS substrates. For demonstrate the hydrophobicity of filter paper SERS substrates with Ag NPs modified by 1-Dodecanethiol, we dropped 3 μ L of deionized water onto the SERS substrate. As shown in Figure 3a, the droplets appeared spherical on the surface of the SERS substrate, which is due to the hydrophobic SERS

substrate could confine the water drop to minimize the contact area. When the SERS substrate is tilted to a certain angle, dropping deionized water onto its surface, it can be observed that the droplet will naturally fall after contacting the surface, rather than being absorbed or diffused on the surface.

The hydrophobicity of paper-based substrates can also be assessed by measuring static water contact angles. The contact angle between 90° and 150° means a hydrophobic surface, and a contact angle greater than 150° corresponds to a superhydrophobic surface. As shown in Figure 3b, after decorating 1-Dodecanethiol, the filter paper-Ag exhibits the excellent hydrophobic feature with a contact angle of 130.2° . The contact angle of a common hydrophobic solid surface was from 100° to 120° . Thus, the fabricated SERS substrate modified by 1-Dodecanethiol shows excellent hydrophobicity, which can prevent the rapid absorption and diffusion of aqueous analyte solutions.

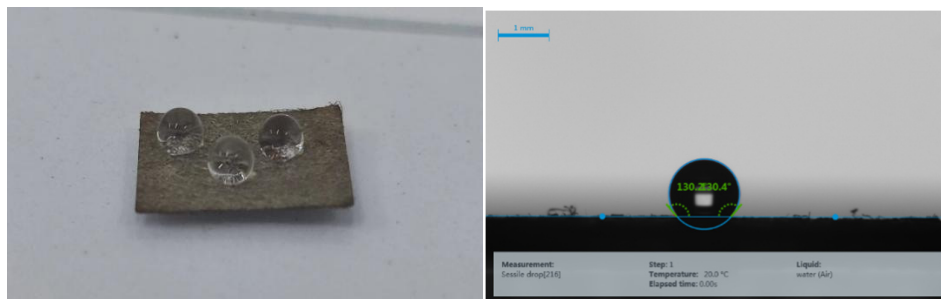


Figure 3. (a) Water drops on hydrophobic SERS substrate, (b) Water contact angle (WCA) of hydrophobic SERS substrate.

3.4. UV-Vis Spectra Analysis of the Substrate

The significant advantage of the SERS substrate prepared through filter paper is that it could be cut into any shape during the experimental process. The appearance of the untreated filter paper sample is white, while filter paper-Ag is grayish green. UV-vis spectroscopy is commonly used to study the optical properties of hydrophobic SERS substrates. Due to the localized surface plasmon resonance (LSPR) of Ag NPs, the absorption bands are mainly located between 360 and 420 nm. The size and shape of Ag NPs on the surface of hydrophobic SERS substrate determine the characteristics of LSPR. As shown in Figure S2, the untreated filter paper sample has no absorption peak, while the hydrophobic SERS substrate has a clear broad peak at 400 nm. This result is consistent with the SEM data.

3.5. FTIR Analysis of the Substrate

As shown in Figure S3, the surface functional groups of filter paper, filter paper-Ag before and after modification with 1-Dodecanethiol were determined by ATR infrared spectroscopy. Several obvious absorption peaks were observed at 3332 cm^{-1} , 2902 cm^{-1} and 1033 cm^{-1} . The peak at 3332 cm^{-1} is assigned to the stretching vibration of OH, the peak at 2902 cm^{-1} is the stretching vibration of C-H, and the peak at 1033 cm^{-1} is the stretching vibration of C-O-groups [31]. After decorating Ag NPs on the surface of filter paper, there is nearly no difference in ATR spectra compared to the original filter paper. That is due to the Ag NPs having no obvious adsorption in IR spectra. After modification with 1-Dodecanethiol, two obvious peaks were measured at 2850 cm^{-1} and 2920 cm^{-1} . The peak at 2850 cm^{-1} is due to the symmetric stretching vibration of methylene, and the peak at 2920 cm^{-1} is due to the asymmetric stretching vibration of methylene [32,33]. The obvious methylene group was originated from 1-Dodecanethiol that grafted on the surface of filter paper-Ag. The ATR result further confirms the hydrophobic feature was due to the hydrocarbon chain.

3.6. Thermogravimetric Analysis

The thermal feature of filter paper and hydrophobic filter-Ag SERS substrate were measured by thermogravimetric (TG) analysis, in which the temperature ranged from 30°C to 600°C . The TG

curves are shown in Figure S4, in which these two materials exhibit similar thermal feature. Obviously weight loss observed at 293 °C and 291 °C for filter paper and hydrophobic SERS substrate, that was because the decompose of paper. There are significant mass losses observed at 530 °C and 488 °C corresponding to filter paper and hydrophobic filter SERS substrate. The filter paper is almost complete pyrolysis, and the residual weight of hydrophobic filter-Ag is nearly 2.5 wt%, which belonging to Ag NPs.

3.7. Application of the Hydrophobic SERS Substrate

In order to evaluate the superior property of hydrophobic SERS substrate, 3uL aqueous solution of R6G(10^{-5} M) were dropped onto the filter paper-Ag before and after grafting 1-Dodecanethiol, respectively. As shown in Figure 4c, there are no fluorescence image observed as the liquid drop was diffused on the common filter paper-Ag. The corresponding SERS spectra as shown in Figure 4a, only weak signal of R6G observed at 10^{-5} M concentration. In contrast, after grafting 1-Dodecanethiol, the obvious fluorescence of R6G was obtained on the surface of hydrophobic filter paper-Ag (Figure 4d). In that case, the droplet of R6G could stay on the hydrophobic surface of substrate. And the Raman spectra of R6G (10^{-8} M) could be observed (Figure 4b). The hydrophobic feature of the filter SERS substrate not only enhanced the SERS spectra of target, but also improve the fluorescence visible effect.

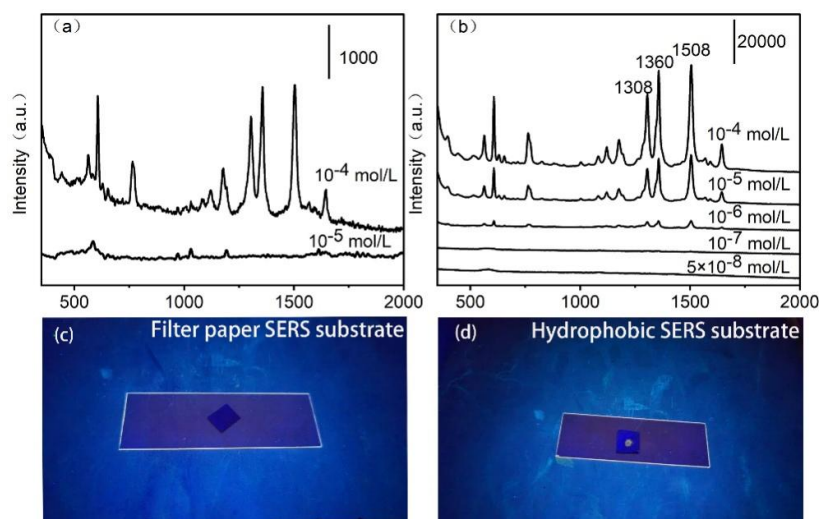


Figure 4. Raman spectra of R6G measured from filter paper-Ag (a) and hydrophobic filter paper-Ag (b), and the corresponding images under UV light (c,d).

3.8. Melamine and Thiram Detection

Melamine has been illegally added to dairy products, causing serious damage to the human health[34]. There are pesticide residues in food stuff during the agricultural production, which pose a serious threat to human health[35]. The hydrophobic SERS substrates were used to monitor melamine and thiram at different concentrations. The Raman spectra of melamine measured from hydrophobic SERS substrate is shown in the Figure S5a. The characteristic peak of melamine was observed at 680 cm^{-1} [36], that attributed to the in-plane deformation mode of triazine ring[37]. The SERS spectra of thiram was shown in Figure S5b, in which several characteristic peak were observed at 559 cm^{-1} , 927 cm^{-1} , 1144 cm^{-1} , 1380 cm^{-1} , and 1503 cm^{-1} . The peak at 559 cm^{-1} is attributed to the stretching vibration of S-S, while the peak at 1144 cm^{-1} is attributed to the swinging vibration of CH_3 and the stretching vibration of C-N. The peaks at 1380 cm^{-1} and 1503 cm^{-1} are attributed to the stretching vibration of CH_3 and $\text{C}=\text{N}$ [38]. That results verified that the hydrophobic filter paper SERS substrate could be used for detecting melamine and thiram.

3.9. Sensing Pesticide from Oil Phase

The hydrophobic filter paper-Ag were applied for monitoring pesticide in real food sample. The thiram was artificially added into edible oil, and 3 μL oil sample with different concentration of thiram were dropped onto the surface of hydrophobic filter paper-Ag. The Raman spectra of thiram measured from oil is shown in Figure 5a, in which the characteristic peak of thiram was observed. And the feature band at 1380 cm^{-1} could still be observed as the concentration down to 10^{-7} M . In order to detect thiram from oil in quantitative way through Raman spectrum, the curve was built between the concentration of thiram and peak intensity at 1380 cm^{-1} (Figure 5b) with coefficient of determination (R^2) at 0.9535. The filter paper substrate without hydrophobic surface was also used to detect thiram from edible oil, unfortunately, there was no feature peak of thiram was obtained (Figure 5c). Because the phase separation would happen as hydrophobic oil contact with hydrophilic surface of SERS substrate. The two phase prevented the interaction between thiram and plasmonic SERS substrate.

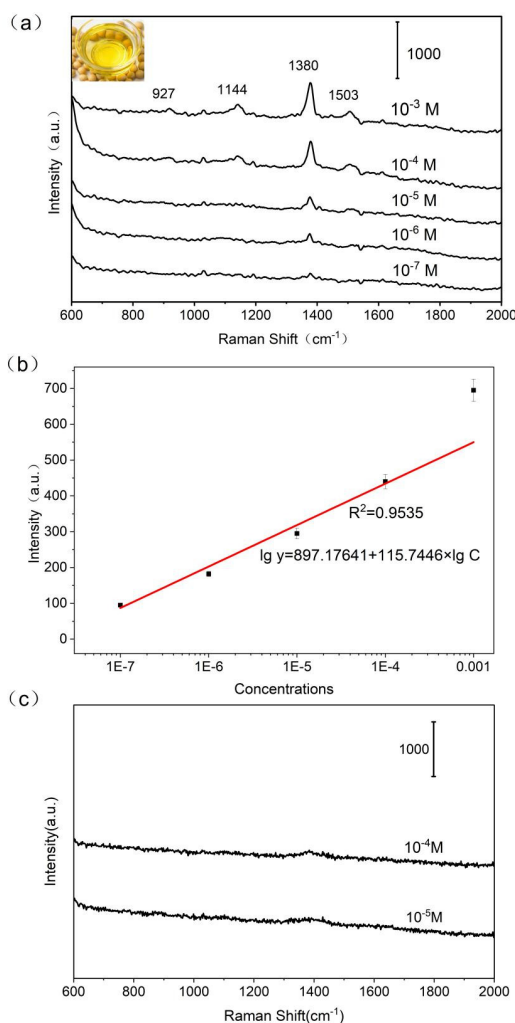


Figure 5. The Raman spectra of thiram measured from edible oil by filter paper substrate with (a) and without (c) hydrophobic surface, and dose-response curves of the Raman peaks at 1380 cm^{-1} (b).

In summary, we proposed a convenient, cost-effective and simple method for fabricating hydrophobic filter paper SERS substrate. The Ag NPs were decorated on the surface of filter paper via in situ growth process, and the 1-Dodecanethiol was grafted onto the surface of filter paper-Ag to prepare hydrophobic filter paper SERS substrate. The contact angle of the hydrophobic filter paper SERS substrate could achieve 130.2°. The hydrophobic feature of the SERS substrate could confine the aqueous sample in certain area, that not only improve the intensity of Raman spectra but also enhance the fluorescence effect. The concept validation detection of hydrophobic SERS substrate was validated by detecting melamine and thiram in aqueous solution. Furthermore the hydrophobic filter paper SERS substrate was successfully employed for sensing thiram from edible oil, in which the superior performance was obtained compared with the filter paper SERS substrate without hydrophobic surface. The hydrophobic filter paper SERS substrate have a great potential for trace detection in SERS sensing.

Supplementary Materials: The following supporting information can be downloaded at the website of this paper posted on Preprints.org.

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Declarations: The authors declare that they have no conflict of interest.

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