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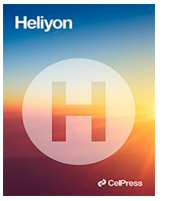

Flexible, high-performance and facile PVA/cellulose/Ag SERS chips for in-situ and rapid detection of thiram pesticide in apple juice

Anh-Tuan Pham [a,b,*,1], Hanh Nhung Bui [b,1], Quan-Doan Mai [c,**,1], Anh-Tuan Le [b,c,***]

[a] Faculty of Biotechnology, Chemistry and Environmental Engineering, Phenikaa University, Hanoi, 12116, Viet Nam
[b] Faculty of Materials Science and Engineering, Phenikaa University, Hanoi, 12116, Viet Nam
[c] Phenikaa University Nano Institute (PHENA), Phenikaa University, Hanoi, 12116, Viet Nam

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ABSTRACT

Flexible surface-enhanced Raman scattering (SERS) sensors have gained significant attention for their practical applications in detecting chemical and biological molecules. However, the fabrication of flexible SERS chips is often complex and requires advanced techniques. In this study, we present a simple and rapid method to design a flexible SERS chip based on polyvinyl alcohol (PVA), cellulose, and silver nanoparticles (AgNPs) using mechanical stirring and drying methods. Benefiting from the abundant hydroxide groups on cellulose, AgNPs easily adhere and distribute evenly on the cellulose surface. The combination of PVA and cellulose forms a bendable film-like SERS chip. This chip allows convenient immersion in liquid analyte samples. We demonstrate its effectiveness by using it to detect the thiram pesticide in apple juice using the "dip and dry" method, achieving an outstanding detection limit of 1.01×10^{-8} M. The Raman signals on the SERS chips exhibit high repeatability and reproducibility, with relative standard deviation values below 10%. These findings show that the flexible PVA/cellulose/Ag SERS chips is a strong candidate for real-world analysis.

1. Introduction

Since its discovery, surface-enhanced Raman scattering (SERS) as an effective and sensitive vibrational spectroscopy analysis tool has been attracting significant attention and showcasing remarkable advancements [1–3]. Due to their ultrahigh sensitivity, noninvasive analysis rapidity, fingerprint recognition, and cost-effectiveness, SERS is widely embraced in various applications, including cancer diagnosis, pharmaceutical quality evaluation, environmental pollutant detection (water, soil, air), and food safety [2–4]. Fundamentally, the SERS effect is explained and widely accepted through two mechanisms: chemical mechanism (CM) and

* Corresponding author. Faculty of Biotechnology, Chemistry and Environmental Engineering, Phenikaa University, Hanoi, 12116, Viet Nam.
** Corresponding author.
*** Corresponding author. Faculty of Materials Science and Engineering, Phenikaa University, Hanoi, 12116, Viet Nam.
E-mail addresses: fattuan@phenikaa-uni.edu.vn (A.-T. Pham), doan.maiquan@phenikaa-uni.edu.vn (Q.-D. Mai), tuan.leanh@phenikaa-uni.edu.vn (A.-T. Le).
[1] A.T.Pham, H.N.Bui and Q.D.Mai contributed equally to this work.

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electromagnetic mechanism (EM) [5,6]. These mechanisms result in a tremendous enhancement of Raman scattering from analytes when they are in close proximity to the surface or within the electromagnetic field of nanoplasmonic materials (Au, Ag, Cu …) [5,6]. Therefore, it is critical to develop nano-based SERS substrates with high effectiveness to enhance the Raman signal. SERS substrates consist of two essential components: (i) nanomaterials that induce plasmon resonance and (ii) a supporter. The common approach involves depositing nanoplasmonic materials onto solid supports like glass, silicon, or aluminum [7–11]. For instance, Chiang et al. successfully utilized a sputtering method to grow Ag films on glass substrates, enabling the impressive detection of crystal violet with a limit of detection of 10^{-11} M [7]. Iarossi et al. ingeniously engineered Au nanopyramid arrays on glass substrates for cell monitoring [8], while Tu et al. demonstrated the direct growth of Ag nanoparticles on silicon wafers, achieving remarkable sensitivity in detecting Rhodamine 6G dye (10^{-11} M) [9]. To enhance reusability and immobilize Ag nanoparticles, Tao et al. fabricated zinc oxide nanorods on silicon wafers and subsequently assembled Ag nanoparticles, resulting in a substantial enhancement factor of 10^7 [10]. In our research reported in 2021, we successfully deposited Ag and Au nanoparticles onto aluminum substrates, enabling the impressive detection of methylene blue with a limit of detection of 5×10^{-12} M in standard samples [11]. Despite their high sensitivity, rigid substrates have limited practicability in solid and gas-phase analysis and face challenges with complex liquid samples, such as fruit juices or industrial wastewater.

Flexible SERS substrates, as an emerging technique, offer remarkable advantages, including their adaptability to curved sample surfaces, as well as the ability to be fully immersed in solutions for enhanced adsorption. Consequently, they have garnered significant interest and extensive research in recent years [12–14]. Diverse flexible substrate materials, such as polymer films, paper, microcellulose, cotton fabric, and adhesive tape, have been extensively explored for designing flexible SERS platforms. For example, Wang et al. reported a new approach by developing a flexible SERS chip, employing a Ternary Film-Packaged Plasmonic Nanoparticle Array. This structure included a poly(methyl methacrylate) (PMMA) template, a polymerase chain reaction adhesive film (qPCR film) for improved plasmonic array durability, and a polyethylene terephthalate (PET) coating on Au@Ag/PMMA/qPCR, acting as a protective barrier to enhance chip stability. The resulting Au@Ag/PMMA/qPCR-PET SERS chip exhibited exceptional sensitivity, enabling the detection of trace amounts of thiabendazole in fruit juice samples with a detection limit of 21 ppb [15]. Another noteworthy study by Lu et al. employed an electrochemical deposition technique to fabricate Ag nanodendrites on a hydrophilic carbon fiber fabric substrate, enabling simultaneous detection of thiram and malachite green (MG) in water samples from lakes with a detection limit of 0.1 ppm [16]. Zhang et al. successfully engineered flexible SERS substrates with polymer nanostructure arrays using advanced roll-to-roll ultraviolet nanoimprint lithography, anodic aluminum oxide (AAO) molds, and Au sputtering on the surface of the polymer nanostructure arrays. This design achieved an impressive enhancement factor of 1.21×10^7 for the detection of Rhodamine 6G [17]. However, it is worth noting that the fabrication of these sophisticated flexible SERS chip substrates entails complex processes, demanding high adhesion and ordered arrangement of nanostructures on flexible materials.

Inspired by those mentioned above, in this study, we aim to fabricate a flexible SERS chips in a simple, rapid, and cost-effective manner based on the design involving three components: (i) nanoplasmonic Ag materials, (ii) microcellulose fibers as the substrate, and (iii) polyvinyl alcohol (PVA) serving as both a connecting agent and a flexible film-forming element. The Ag nanoparticles demonstrate excellent compatibility with the cellulose substrate, resulting in uniform and substantial decoration on the cellulose surface within just 1 h of ambient stirring. The PVA/cellulose/Ag structure is synthesized through a 1-h ambient stirring process. Subsequently, a highly flexible film is formed by evaporating water at 80 °C for 3 h. Notably, the PVA/cellulose/Ag structure, with a 1:1 mass ratio of PVA:(cellulose/Ag), exhibits significantly low water solubility. An evaluation comparing the SERS sensing efficiency of rigid Ag/Al substrate and flexible PVA/Cellulose/Ag SERS chips was conducted for detecting thiram analyte. Although the rigid Al/Ag substrate exhibited higher detection efficiency (LOD = 1×10^{-10} M), the flexible PVA/cellulose/Ag SERS chips still demonstrated impressive sensitivity, with a detection limit of 1.1×10^{-8} M. Furthermore, the flexible chips demonstrated remarkable reliability, with a relative standard deviation (RSD) of repeatability and reproducibility approximately 10%. The practicability of the prepared SERS chips was assessed by detecting thiram in real apple juice samples with concentrations ranging from 1.0×10^{-5} to 1.0×10^{-8} M, achieving excellent recovery values of 97–152%. The "dip and dry" technique was utilized, immersing the PVA/cellulose/Ag chips in standard water and apple juice samples for 1 min, facilitating thiram adsorption on the SERS chips surface. Importantly, the flexible PVA/cellulose/Ag SERS chips was fabricated using a simple and cost-effective method, enabling direct immersion of the chips into the analyte solutions. This straightforward and efficient approach offers a practical solution for future designs of flexible SERS chips.

2. Materials and methods

2.1. Materials

Sodium citrate ($Na_3C_6H_5O_7$, 99.9%), Sodium dodecyl sulfate ($CH_3(CH_2)_{11}OSO_3Na$, 99.0%), Thiram ($C_6H_{12}N_2S_4$, 97.0%) were purchased from Shanghai Chemical Reagent and used directly without further purification. Polyvinyl Alcohol ($[C_2H_4O]_n$, 99%) was supplied from Kuraray Co., Ltd (Singapore). Cellulose ($[C_6H_7O_2(OH)_3]_n$, 99.9%) was purchased from Shandong Zunhong Biotechnology Co., Ltd (China). Two silver plates (purity: 99.99%) were prepared with dimensions of (100 mm × 5 mm × 0.5 mm). Double distilled water was used throughout the experiments.

2.2. Electrochemically synthesized silver nanoparticles and their characterizations

The electrochemical synthesis method was employed to fabricate Ag nanoparticles (AgNPs), following the procedure outlined in our previous study with minor modifications [11]. The synthesis process was conducted in a 200 ml beaker containing a 0.1%

$Na_3C_6H_5O_7$ solution in distilled water, supplemented with 0.1% $CH_3(CH_2)_{11}OSO_3Na$ as a surfactant. Prior to synthesis, the electrodes underwent mechanical polishing and rinsing with distilled water to remove surface oxides. Electrolysis took place at room temperature with continuous stirring at 300 revolutions per minute for 3 h. Subsequently, a dense grayish-yellow solution of AgNPs was obtained. The shape and size of the AgNPs were characterized using a Hitachi S-4800 scanning electron microscope (SEM) operating at an acceleration voltage of 5 kV, revealing spherical nanoparticles with an average diameter of 24 nm. UV–Vis absorption spectrum measurements were performed using a JENWAY 6850 spectrophotometer. The prepared AgNPs exhibited a prominent plasmonic band at approximately 404 nm. Further comprehensive details on the properties of AgNPs can be found in our previous study [11].

2.3. Fabrication of flexible PVA/cellulose/Ag SERS chips

The flexible PVA/cellulose/Ag SERS chip was fabricated using a simple and rapid method of mechanical stirring and drying. Initially, Ag nanoparticles (AgNPs) were dispersed in a water-based solvent (prepared using the electrochemical method described in section 2.2). Subsequently, cellulose was introduced to the colloidal solution of AgNPs and stirred for 1 h, allowing the Ag nanoparticles to adhere to the surface of cellulose (resulting in a color change from white to gray in the cellulose fibers). Following that,

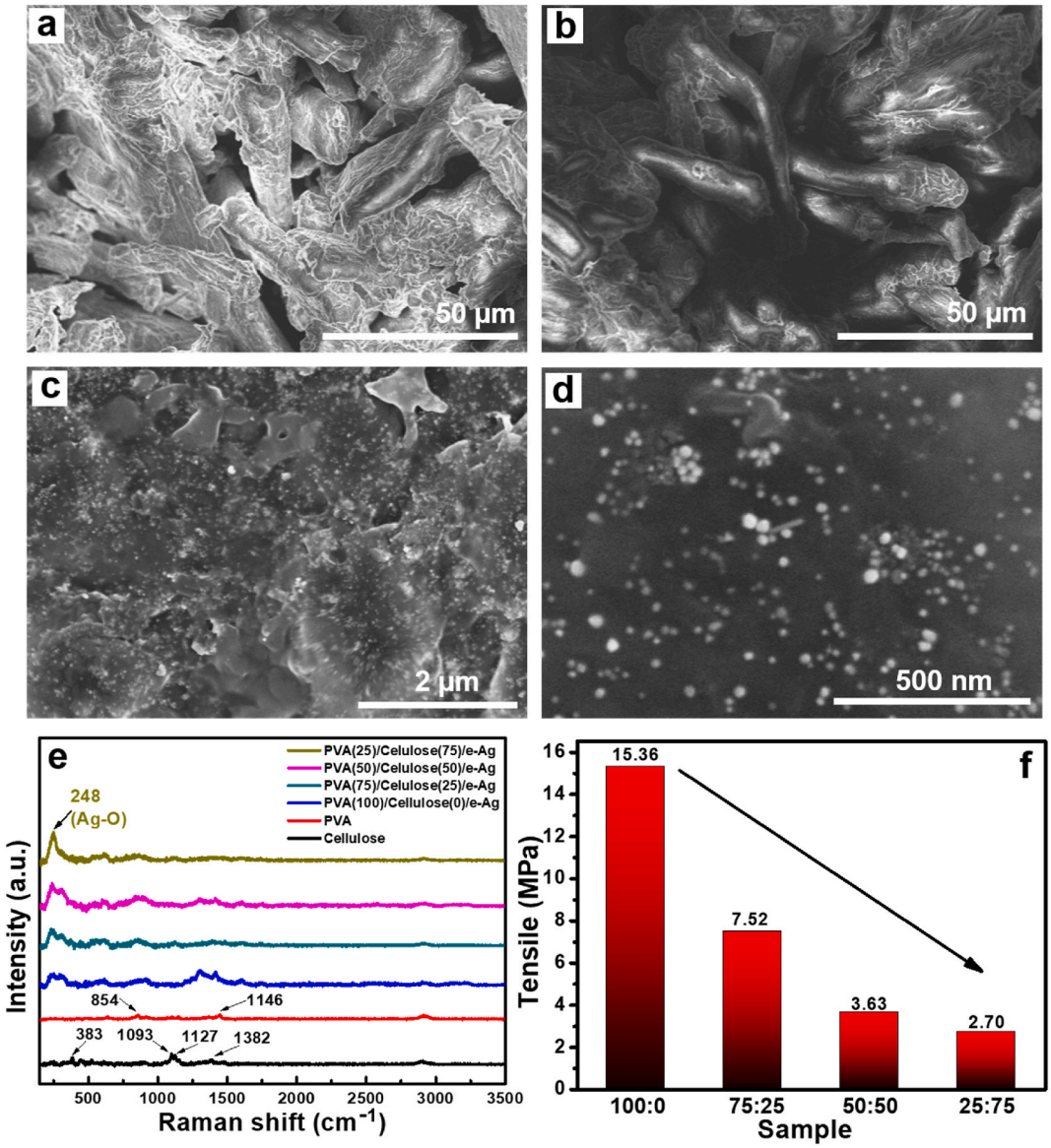

Fig. 1. SEM images of (a) cellulose/Ag and (b,c,d) PVA/cellulose/Ag at different resolutions; (e) Raman spectra of cellulose, PVA and PVA/cellulose/Ag with different ratios of PVA:(cellulose/Ag) content; and (f) tensile strength of PVA/cellulose/Ag with different ratios of PVA:(cellulose/Ag) content.

different weight ratios of PVA:(cellulose/Ag) (75:25, 50:50, and 25:75) were added to the cellulose/Ag mixture and stirred for an additional hour, resulting in a solution mixture of PVA/cellulose/Ag. Finally, the water evaporation process was carried out at 80 °C for 3 h to obtain the flexible PVA/cellulose/Ag SERS chip in the form of a film. Additionally, a PVA/Ag sample was prepared by directly adding PVA to the AgNPs colloidal solution, stirring for 1 h, and evaporating the water, enabling a comparison of its effectiveness with the PVA/cellulose/Ag chips.

2.4. Thiram in distilled water and apple juice: sample collection and SERS measurements

Thiram solutions with varying concentrations (ranging from 1.0×10^{-3} M to 1.0×10^{-9} M) were prepared in distilled water. For each SERS measurement, the flexible PVA/cellulose/Ag SERS chips were immersed in the thiram water solution for 1 min. Subsequently, the chips were removed and dried at a temperature of 40 °C, using the "dip and dry" technique as previously mentioned. The SERS spectra were recorded using a MacroRaman™ Raman spectrometer (Horiba) with a 785 nm laser excitation. Raman measurements were obtained using a 100 × objective lens with a numerical aperture of 0.90. The laser power was set at 45 mW, and the contact angle was maintained at 60°. The laser spot diameter was 1.1 μm (1.22λ/NA), and the focal length was 115 nm. Each measurement had an exposure time of 15 s with a single accumulation. Finally, the baseline was calibrated, and the resulting spectrum was obtained.

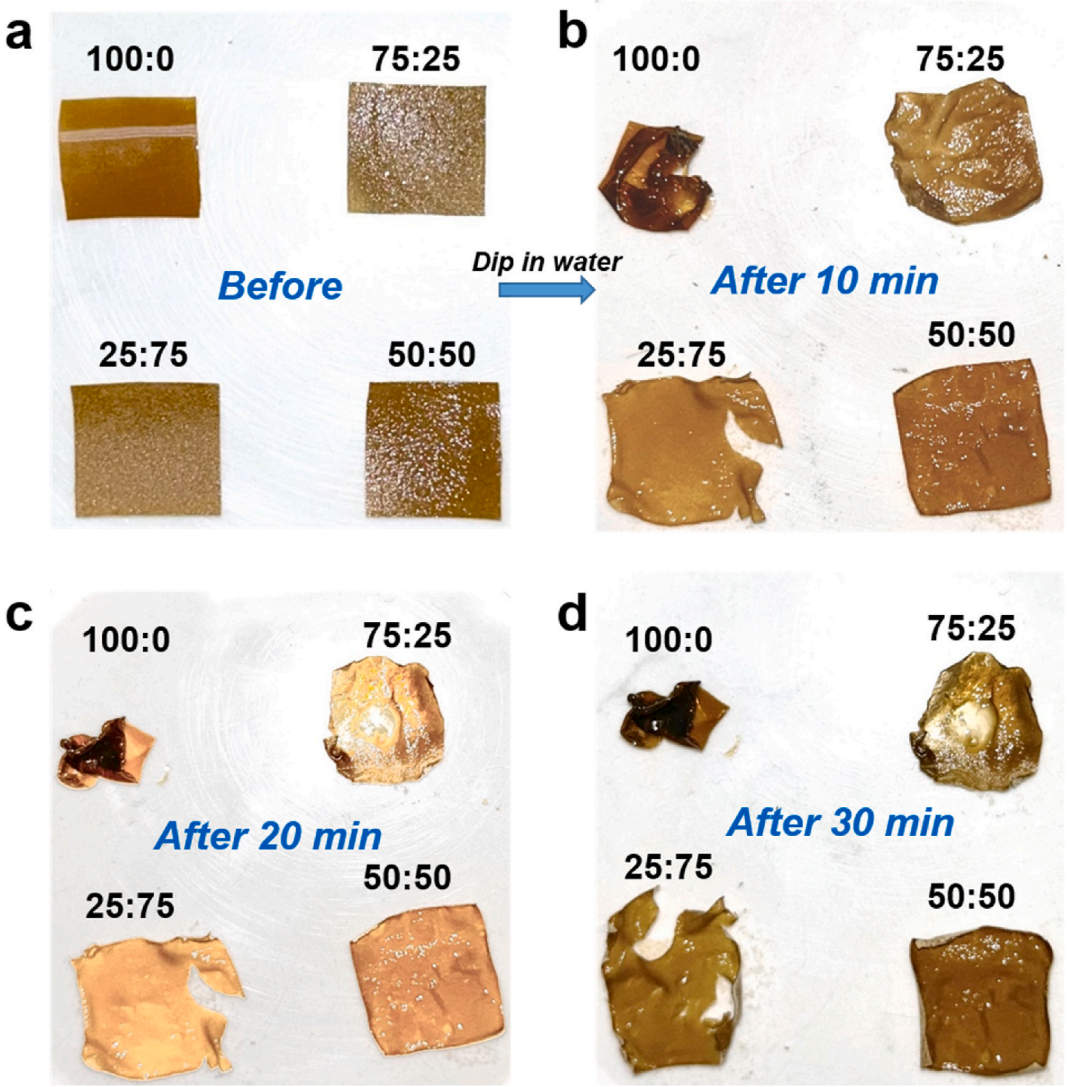

Fig. 2. Solubility of PVA/cellulose/Ag with varying PVA:(cellulose/Ag) ratios including 100:0, 75:25, 50:50, and 25:75 before (a) and at 10 min (b), 20 min (c), and 30 min (d) after water immersion.

2.5. Apple juice real sample: sample collection and SERS measurements

The apple juice was directly purchased from a local supermarket in Hanoi, Vietnam, and used without any processing. Subsequently, apple juice samples with thiram concentrations ranging from 1.0×10^{-5} M to 1.0×10^{-8} M were prepared for SERS experiments. The thiram in the apple juice samples was collected using flexible PVA/cellulose/Ag SERS chips through the "dip and dry" technique. Specifically, the SERS chips were immersed in the thiram-containing apple juice sample for 1 min and then dried at a temperature of 40 °C. These SERS chips were later employed for Raman spectroscopy measurements.

3. Results and discussion

3.1. Fabrication of flexible PVA/cellulose/Ag SERS chips

The flexible PVA/cellulose/Ag SERS chips were easily fabricated by depositing Ag nanoparticles (NPs) onto cellulose fibers after 1 h of stirring, followed by incorporating PVA for chip formation. SERS chips with varying PVA:(cellulose/Ag) weight ratios of 100:0, 75:25, 50:50, and 25:75 were successfully created and thoroughly examined. In the absence of PVA, the cellulose/Ag material failed to form a film-like structure. The SEM image of the cellulose/Ag material (Fig. 1a) revealed cellulose fibers with diameters of approximately 10–15 μm, featuring a rough surface conducive to Ag nanoparticle attachment. Furthermore, the SEM image of the PVA/cellulose/Ag SERS chips (Fig. 1b) exhibited a dense arrangement of cellulose fibers. Notably, the inclusion of PVA did not disrupt the original structure and alignment of the cellulose fibers. At higher resolution (Fig. 1c), the presence of uniformly arranged bright white spherical nanoparticles on the cellulose fiber surface was clearly observed. Fig. 1d provided compelling evidence of the existence of spherical particles, with an average size of 20–25 nm, similar to the Ag NPs. Thus, it can be inferred that the Ag NPs were successfully affixed onto the cellulose surface in a uniform distribution.

Fig. 1e illustrates the Raman spectra of cellulose, PVA, and the flexible PVA/cellulose/Ag SERS chips with varying PVA:(cellulose/Ag) weight ratios. The Raman spectrum of cellulose exhibits scattering peaks at 1093 cm^{-1}, assigned to CC and CO stretching vibrations, 1127 cm^{-1}, indicative of CH, CH_2, and OH stretching vibrations, and 1382 cm^{-1}, associated with HCC, HCO, and HOC bending vibrations within the cellulose structure [18]. The Raman spectrum of PVA displays characteristic peaks at 854 cm^{-1}, corresponding to C–C stretch vibrations, and at 1146 cm^{-1}, representing C–O stretching in the PVA molecular structure [19]. In the Raman spectrum of the PVA/cellulose/Ag SERS chips, a prominent peak is observed at 248 cm^{-1}, which intensifies with increasing cellulose/Ag content. This scattering peak is attributed to the Ag–O stretching mode, potentially formed due to the interaction between Ag NPs and the cellulose surface [20]. The tensile strength of the PVA/cellulose/Ag SERS chips was evaluated, revealing a decreasing trend with higher cellulose/Ag content (Fig. 1f). However, despite the reduction in mechanical strength, the flexibility of the SERS chips remains uncompromised.

PVA is a widely available, low-cost, and easily processed polymer, making it ideal for simple SERS chip fabrication. However, its water solubility presents a challenge for analyses conducted in aqueous environments. Therefore, evaluating the water solubility of PVA/cellulose/Ag chips is crucial for determining their applicability. Fig. 2 shows the water solubility of PVA/cellulose/Ag SERS chips with varying PVA:(cellulose/Ag) ratios, including 100:0, 75:25, 50:50, and 25:75. The initial appearance of these chips is depicted in Fig. 2a. Chips were immersed in water for 2 min, and images were captured at intervals of 10 min (Fig. 2b), 20 min (Fig. 2c), and 30 min (Fig. 2d) after the immersion process. The PVA/Ag (100:0) chip experienced significant shape deformation, losing its film structure. However, the presence of cellulose enhanced stability upon water contact. With 25% cellulose content, the PVA(75)/cellulose(25)/Ag chip maintained its film shape for 10 min but lost structure after 20 min. In contrast, the PVA(50)/cellulose(50)/Ag chip demonstrated superior water stability, maintaining its film shape even after 30 min. However, at 75% cellulose content, the film structure could not be maintained due to low PVA content, resulting in reduced connectivity. Consequently, the PVA(50)/cellulose(50)/Ag SERS chip was selected for subsequent sensor experiments due to its optimal water stability and film integrity. Fortunately, the

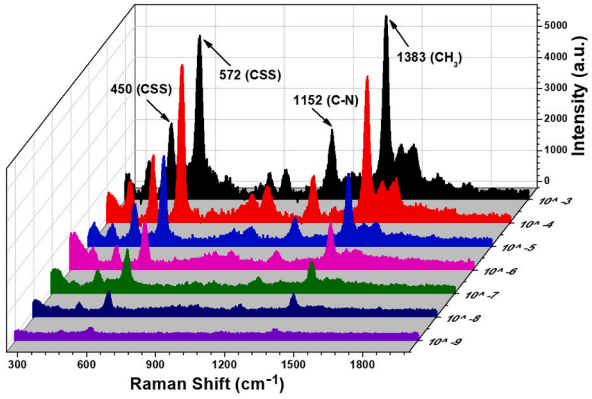

Fig. 3. SERS spectra of thiram solution at different concentrations on rigid Ag/Al substrate.

solubility of the PVA/cellulose/Ag substrates does not significantly affect the SERS sensing experiments. Given their short interaction time with water – only 1 min – followed by immediate drying at 40 °C, they maintain their essential stability.

3.2. Rigid Ag/Al SERS substrate for detection of thiram in distilled water

The SERS sensing efficiency of two types of platforms, rigid and flexible substrates, was evaluated by depositing Ag NPs on an Al substrate as the rigid platform, as detailed in our previous study. The detection capability of the rigid Ag/Al substrate for the thiram pesticide was assessed, and the results are illustrated in Fig. 3. Thiram was dissolved in distilled water at different concentrations and directly applied onto the Ag/Al substrate, followed by natural drying. At a thiram concentration of 1.0×10^{-3} M, distinctive peaks emerged at 450 cm^{-1} (CSS symmetric stretching), 572 cm^{-1} (S–S and CSS symmetric stretching), 1152 cm^{-1} (CH_3 rocking and N–CH_3 stretching), and 1383 cm^{-1} (CH_3 rocking and C–N stretching), which are characteristic vibrational modes of thiram [21–23]. These peaks gradually decreased in intensity as the concentration decreased from 1.0×10^{-3} M – 1.0×10^{-9} M, with a very weak presence observed at 10^{-9} M. The relationship between thiram concentration and SERS intensity was found to be linear, as depicted in Fig. 4. All four peaks, located at 1383 cm^{-1} (Fig. 4a), 1147 cm^{-1} (Fig. 4b), 572 cm^{-1} (Fig. 4c), and 450 cm^{-1} (Fig. 4d), exhibited strong linearity, as evidenced by linear regression coefficients (R^2) exceeding 0.96. Among these peaks, the 1383 cm^{-1} peak displayed the highest R^2 value of 0.99 and was selected to establish the linear range and limit of detection. The limit of detection was determined to be 1.1×10^{-10} M.

3.3. Flexible PVA/cellulose/Ag SERS chips for detection of thiram in distilled water: "dip and dry" collection

The SERS sensing efficiency of the flexible PVA/cellulose/Ag chip for thiram detection was evaluated in a concentration range of 1.0×10^{-5} M – 1.0×10^{-8} M, which was determined as the linear range using the rigid Ag/Al substrate. In contrast to the conventional method of applying the analyte onto a rigid SERS substrate, the flexible PVA/cellulose/Ag SERS chips were immersed directly into a solution containing thiram for 1 min, allowing the thiram molecules to adsorb onto the chip's surface. Afterward, the chip was air-dried at room temperature (called the "dip and dry" technique) (Fig. 5b). The results are presented in Fig. 5a, showing distinct and well-defined characteristic peaks of thiram at positions 450, 572, 1127, and 1383 cm^{-1} at a concentration of 1.0×10^{-5} M. These characteristic peaks remained clearly observable at concentrations of 1.0×10^{-6} and 1.0×10^{-7} M, while displaying weaker signals at a concentration of 1.0×10^{-8} M. The flexible PVA/cellulose/Ag chips possessed a limit of detection of 1.01×10^{-8} M, demonstrating excellent detection ability. Furthermore, the reliability of the PVA/cellulose/Ag chip was assessed for repeatability and reproducibility. Because the PVA/cellulose/Ag chip was fully immersed in the thiram water solution for 1 min, and thiram adsorption onto the substrate occurs randomly, it is important to examine the SERS signal intensity at various points on the substrate. Repeatability was evaluated by measuring at five different positions on a chip detecting thiram at a concentration of 1.0×10^{-5} M, resulting in a relative standard deviation (RSD – using equation in Supporting information) value of 9.84% (Fig. 5c). Another essential requirement is for the PVA/cellulose/Ag chips to consistently exhibit detection capability across various fabrications, ensuring experimental accuracy.

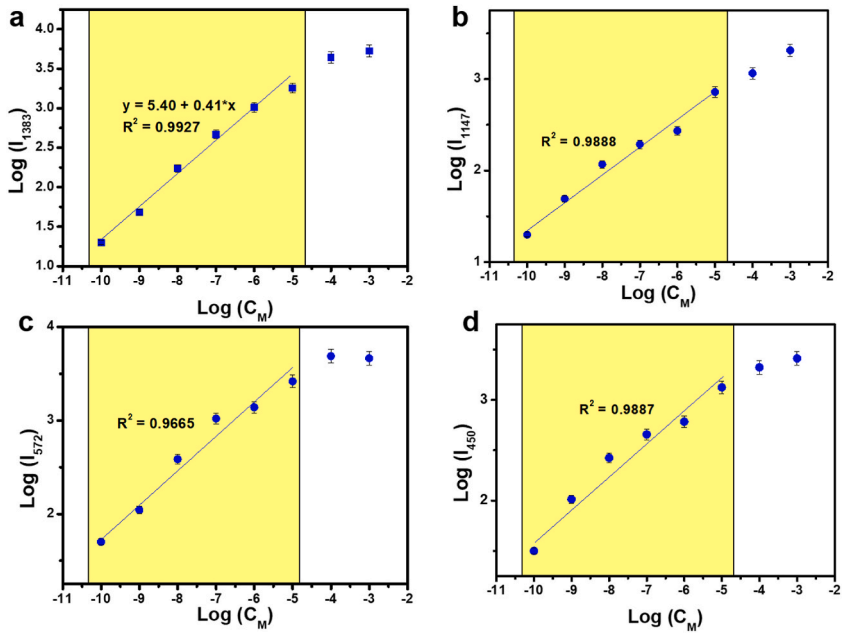

Fig. 4. Plot of log of SERS intensity at (a) 1383 cm^{-1} (slope 0.41 ± 0.01, intercept 5.40 ± 0.05, $R^2 = 0.99$), (b) 1147 cm^{-1} ($R^2 = 0.98$), (c) 572 cm^{-1} ($R^2 = 0.96$), and (d) 450 cm^{-1} ($R^2 = 0.98$).

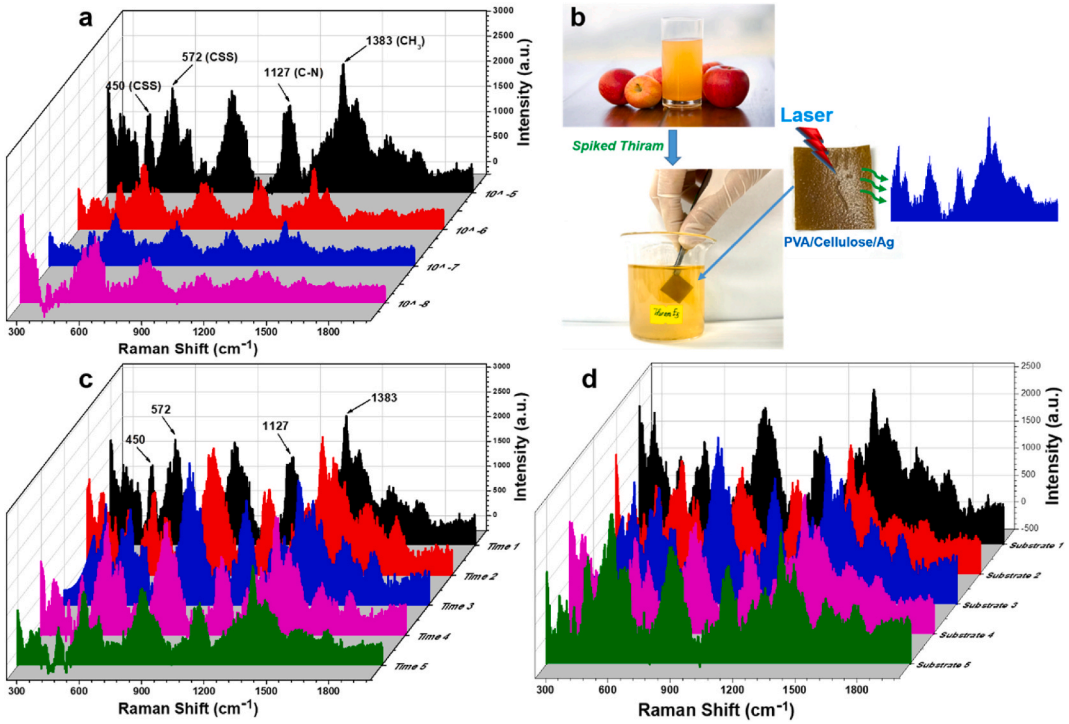

Fig. 5. (a) SERS spectra of thiram solution at different concentrations on flexible PVA/cellulose/Ag chips, (b) "Dip and dry" method to collect thiram in apple juice, (c) repeatability and (d) reproducibility of the SERS sensor for thiram detection based on flexible PVA/Cellulose/Ag chips.

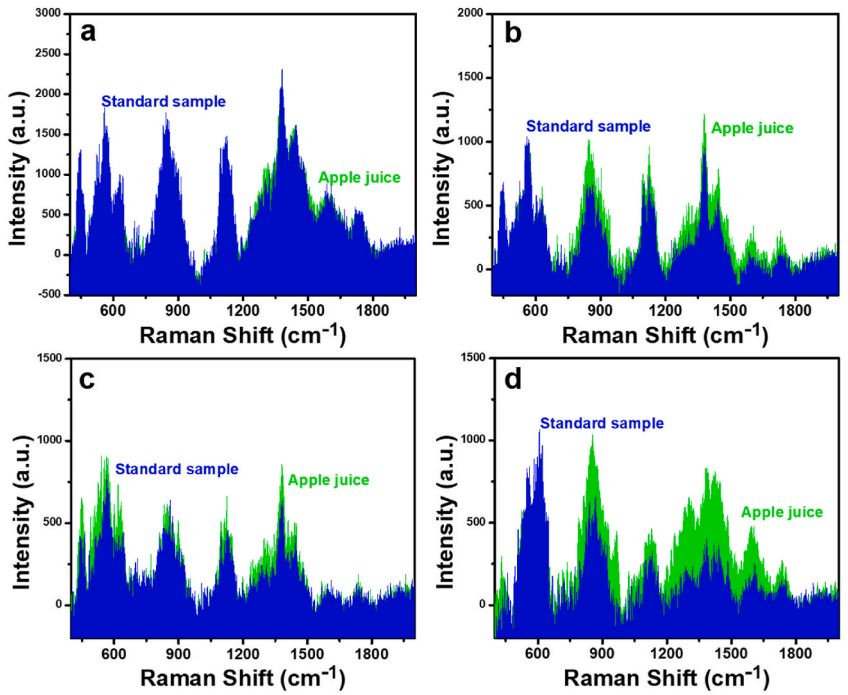

Fig. 6. Comparison of SERS spectra from flexible PVA/Cellulose/Ag SERS substrate for thiram detection in distilled water (blue) and apple juice (green) at different concentrations, including a concentration of 10^{-5} M (a), 10^{-6} M (b), 10^{-7} M (c), and 10^{-8} M (d).

Reproducibility was evaluated by fabricating five different PVA/cellulose/Ag chips and detecting thiram at a concentration of 1.0×10^{-5} M, yielding an RSD value of 2.22% (Fig. 5d). The high repeatability and reproducibility (RSD <10%) highlight the strong potential for practical applications of the PVA/cellulose/Ag chips.

3.4. Flexible PVA/cellulose/Ag SERS chip for detection of thiram in apple juice: "dip and dry" collection

The practicability of the flexible PVA/cellulose/Ag SERS chip was assessed using the "dip and dry" technique for detecting thiram in apple juice samples. Various concentrations of thiram (10^{-5} M, 10^{-6} M, 10^{-7} M, and 10^{-8} M) were spiked into the apple juice. The obtained SERS spectra from the flexible PVA/cellulose/Ag SERS chip (green) were compared to those from thiram detection in distilled water (blue), as shown in Fig. 6a, b, 6c, and 6d with concentrations of 10^{-5}, 10^{-6}, 10^{-7}, and 10^{-8} M, respectively. The results demonstrate the excellent ability of the flexible PVA/cellulose/Ag SERS chip in detecting thiram in apple juice samples, even in the presence of complex juice matrices. Regardless of the matrix complexity, the chip consistently displayed accurate thiram detection. Furthermore, the recovery values were calculated (using equation (1)), yielding percentages of 97%, 119%, 108%, and 152% for concentrations of 1.0×10^{-5} M, 1.0×10^{-6} M, 1.0×10^{-7} M, and 1.0×10^{-8} M, respectively. The recovery rate of each measurement is calculated using the equation:

$$\text{Recovery } (\%) = \frac{\text{Spiked analyte concetration (M)}}{\text{Calculated analyte concetration (M)}} \times 100\ \% \quad (1)$$

These recovery percentages indicate the chip's ability to precisely quantify thiram levels in the tested concentrations. Overall, the flexible PVA/cellulose/Ag SERS chip proves to be practical and effective for thiram detection in apple juice samples, showcasing its potential for real-world applications.

Compared to similar studies, Table 1 presents the sensor performance and sample collection techniques of SERS substrates based on AgNPs. The Au@Ag nanostructure, decorated on a GO-modified quartz slide, has demonstrated its ability to detect thiram in apple juice, achieving a LOD of 36.7 ng/ml (~1.53×10^{-7} M) [24]. However, the inherent rigidity of the quartz substrate required the "liquid droplet" technique, which involves dropping apple juice onto its surface. As previously discussed, this method can pose challenges in environments with complex chemical compositions. In another study, cotton swabs were coated with AgNPs, taking advantage of their flexibility to swipe across apple skins for thiram detection, with results indicating a LOD of 0.53 ng/cm^2 (~2.21×10^{-12} mol/cm^2) [25]. Nonetheless, the potentially non-uniform structure of these commercial swabs can lead to inconsistent results, as evidenced by a reproducibility value reaching up to 19.37%. A study close to ours [26] utilized nanocellulose fibers coated with AgNPs to detect thiram on apple surfaces via the "paste and peel off" method, achieving a LOD of 0.5 ng/cm^2 (~2.08×10^{-12} mol/cm^2). This substrate, however, with its jellylike state, required a rigid Al substrate for SERS measurements. Such a design limits its wider applicability; when exposed to solvents, its structure is prone to deterioration. In contrast, our substrate, when integrated with PVA, results in a stable PVA/Cellulose/Ag film. Combined with a uniform distribution of AgNPs on the cellulose, our approach attained a remarkable LOD of 1.01×10^{-8} M (~1.01×10^{-11} mol/cm^3) in apple juice using the "dip and dry" technique, showcasing impressive repeatability (RSD = 9.84%) and reproducibility (RSD = 2.22%).

4. Conclusions

In this study, we successfully fabricated flexible PVA/cellulose/Ag SERS chips using a simple, rapid, and cost-effective method of mechanical stirring and drying. The 1:1 wt ratio of PVA:(cellulose/Ag) chips exhibited high flexibility and low water solubility. By directly immersing the chips in thiram solution using the "dip and dry" technique, we achieved an impressive thiram limit of detection of 1.01×10^{-8} M. The chips demonstrated excellent reliability with RSD values of 2.22% and 9.84% for reproducibility and repeatability, respectively. Furthermore, they effectively detected thiram in real apple juice samples without any pretreatment, providing recovery values ranging from 97% to 152%. The simple, rapid, and cost-effective fabrication process of the PVA/cellulose/Ag SERS chips, combined with their flexibility for direct analyte analysis in real samples, simplified the entire analytical process. This study presents a straightforward and efficient approach for designing and fabricating flexible SERS chips with practical applications.

Author contribution statement

Anh-Tuan Pham: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Hanh Nhung Bui: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Quan Doan Mai: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Anh-Tuan Le: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Data availability statement

Data will be made available on request.

Table 1
Comparing sensor performance and sample collection techniques for thiram detection in/on apple samples using AgNP-based SERS substrates (graphene oxide (GO), nanoparticle (NP)).

	Substrate	Sample collection	LOD	Repeatability (RSD %)	Reproducibility (RSD %)	Ref.
Au@Ag NP GO composite	quartz slide	"liquid droplet"	36.7 ng/ml	6.66–13.89	–	[24]
AgNPs	cotton swab	"swabbing"	0.53 ng/cm^2	–	< 20	[25]
AgNPs-decorated nanocellulose	aluminum plate	"paste and peel off"	~0.5 ng/cm^2	9.19	10.27	[26]
PVA/Cellulose/Ag	PVA	"dip and dry"	1.01×10^{-8} M	9.84	2.22	*this work*

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:Anh-Tuan Le reports administrative support and equipment, drugs, or supplies were provided by Phenikaa University.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.heliyon.2023.e19926.

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