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A novel paper rag as 'D-SERS' substrate for detection of pesticide residues at various peels

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ABSTRACT

Many important considerations in the design of practical Surface enhanced Raman spectroscopy (SERS) substrates are necessary, such as the low cost, simple preparation, mass production and high efficiency of sample collection, which the conventional rigid substrates are lack of. In this work, practical SERS substrates based on deposition of silver nanoparticles (Ag NPs) on commercially available low-cost filter paper were prepared by simple silver mirror reaction in a large scale, and utilized for rapid, portable and accurate identification and detection of pesticide residues at various peels. Compared with conventional substrates, this novel SERS substrate dramatically enhanced the sample collection efficiency by simply swabbing paper-based device across different surfaces without destroying the sample, meanwhile avoiding the substrate signal of real-world samples. Considering their low cost, portability, simplicity and high sample collection efficiency, Ag NP-decorated filter paper, as practical SERS substrate, are used in solving critical problems for detection of pesticide residues at various peels. SERS experiments were carried out on Ag NP-decorated filter paper combined with 'dynamic SERS' (D-SERS) due to its high detection sensitivity. The excellent detection performance of the Ag NP-based filter paper was demonstrated by detection thiram and paraoxon residues at various peels. Besides, the stability and reproducibility of the practical substrates were also involved.

1. Introduction

Many attempts have been made to promote the rapid application of Surface enhanced Raman spectroscopy (SERS) substrate in various fields, including analytical chemistry, medical science, environmental monitoring, explosives analysis and so on [1–6]. From the application viewpoint, there still remains numerous considerations in the design of practical SERS substrates. As we know, most of conventional SERS substrates are based on silicon wafer, glass wafer, and porous alumina [7–10], which exist more or less drawbacks as a practical SERS substrate, such as high price, sophisticated preparation and treatment process. However, paper-based SERS device are compatible with the demands for practical SERS substrates owing to the low cost, portability, simplicity and flexibility of paper [11–12].

Many attempts were made to synthesize varieties of paper-based SERS device in recent years. There are three main routes to fabricate paper-based substrates: (i) the most used strategy is ink-jet-printed method [13–18]. In general, Ag or Au nanoparticles were prepared by following the method of Lee and Meisel [19], nanoparticle colloids were then printed on filter paper to form the paper-based substrates. (ii) Another path to fabricate paper-based device is that a piece of filter paper was dipped into multiple nanostructures of Au gels prepared previously, such as nanoparticles [20,21], nanorods [22] and bipyramids [23], making the nanostructures simply adsorbed on the paper. (iii) The physical way is to use the photothermal effect to prepare metal nanoparticle-containing test papers [24]. Heating and complex prerequisites were needed in synthesizing the nanostructures among these chemical reaction methods, whereas high cost is inevitable to fabricate paper device by physical way. Considering many issues still associated with SERS substrates, there is a need for developing a sensitive, cost-efficient, uniform, and easily prepared SERS substrate.

Controlling the hot spots for maximizing electromagnetic enhancement to obtain the strongest SERS signals have been a major research interest over the past few decades [25–29]. In recent years, our group have made many efforts to research the hot spots by D-SERS method. D-SERS is a new kind of analytic technique to collect Raman signals during the SERS substrate transition process from wet state to dry state [30]. Specifically, the nanoarrays are brought very close driven by the capillary force of solvent evaporation, thus SERS hot spots can

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spontaneously form, at the same time the target analytes can also be trapped in the nanoarrays via the solvent capillary force. As a result, SERS signals are greatly enhanced. When solvent disappeared thoroughly, nanostructures changed back to their original positions, meaning that hot spots disappeared. It is very important that the process is recyclable and reproducible, i.e., the solvent can act as a switch for SERS detection. D-SERS method owns high detection sensitivity and reproducibility due to forming plenty of hot spots and the volatilization-induced automatic concentration of the target molecule during the detection process [31–33]. On the basis of above D-SERS description, our strategy is to expand this concept and to realize 'D-SERS' (different from traditional D-SERS method) detection for substrates with fixed nanoparticles. This 'D-SERS' technique comes from the analytes concentration, movement of analytes molecules and increasing frequencies of analytes molecules colliding with substrate during the solvent evaporation process. Considering molecule trapping and SERS sensing with high sensitivity and uniformity, 'D-SERS' technique can help us to make SERS a practical analytical technique.

In this work, we fabricated a practical SERS substrate in a large area made up of Ag NPs decorated filter paper via simple silver mirror reaction at room temperature without complex reaction process. Except for advantages of low cost and simple preparation for Ag NP-decorated paper, the paper-based platform combined with 'D-SERS' technique used for the rapid detection of pesticide residues in the real-world samples has many superiorities. On the one hand, the hot spots from nanostructures and concentrated target molecule can be formed during solvent evaporation process; consequently, high sensitivity and reproducibility can be acquired by 'D-SERS' method in the practical applications. On the other hand, the prepared paper substrate can act as a rag to collect samples in real world, which are incredibly difficult to rigid substrates. Here, pesticide residues were collected by simply swabbing the paper substrate across a wide-area surface of peels. Detection performance was explored by detection thiram and paraoxon residues at various peels, such as apples, bananas and tomatoes.

2. Experiment details

2.1. Chemicals and materials

All chemicals used in this experiment were analytical grade and used without further purification. $AgNO_3$, $NH_3 \cdot H_2O$, HCHO were purchased from Shanghai Chemical Reagent Company (Shanghai, China). Double-distilled water ($> 18.0\ M\Omega\ cm$) was purified using a Millipore Milli-Q gradient system throughout the experiment.

2.2. Characterization

Field emission scanning electron microscopy (FESEM) images were taken on a FESEM (Quanta 200FEG) operated at an accelerating voltage of 10.0 kV. X-ray photoelectron spectroscopy (XPS) analyses of the samples were conducted on a VG ESCALAB MKII spectrometer using an Mg Ka X-ray source (1253.6 eV, 120 W) at a constant analyzer. Raman spectra of pesticide molecules were carried out on an inspector microscope Raman system (DeltaNu) operating at 785 nm. The laser power was approximately 30 mW. The accumulation time for each spectrum reported was10 s.

2.3. Fabrication of AgNPs on filter paper

Silver mirror reaction method was introduced to construct Ag NPs on filter paper as SERS substrates. In brief, 2% $NH_3 \cdot H_2O$ was dropwised into 20 mL 5 mM aqueous $AgNO_3$ until yellow precipitate disappeared, the silver ammonia solution was kept in a petri dish and common laboratory filter papers without any pretreatment were immersed in the solution for few minutes to keep Ag $(NH_3)_2^+$ adsorbed on the surface of the filter paper. 10% formaldehyde solution was then added and silver mirror reaction happened at room temperature. After the reaction was finished, the paper was taken out from the solution and washed with deionized water,

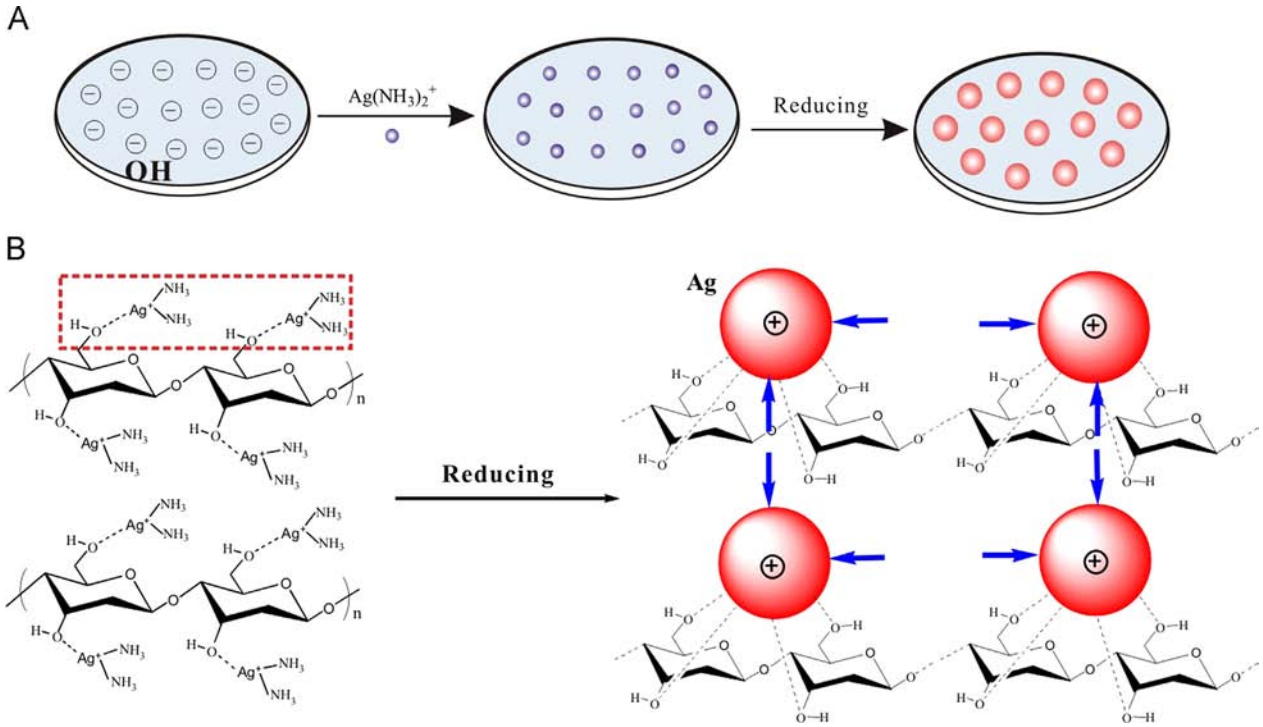

Fig. 1. (A)Schematic representation of formation mechanism of Ag NP-decorated filter paper, and (B) the possible adsorption interactions between $Ag(NH_3)_2^+$ and cellulose fibre, and interactions on the Ag NP-based filter paper.

ethanol and formaldehyde successively. The paper was dried in the air at room temperature.

2.4. Storage of Ag NP-decorated filter paper

After the preparation and drying of Ag NP-decorated filter paper, the paper substrate was kept in a petri dish and conserved in the air without any treatment for many days.

3. Results and discussion

3.1. in situ fabrication and characterization of Ag NPs-decorated filter paper

Here, we introduced a convenient and eco-friendly procedure to fabricate high density and uniform Ag NPs on filter paper by simple silver mirror reaction. Formation process of Ag NP-decorated filter paper is shown in Fig. 1A. A piece of filter paper was immersed into $Ag(NH_3)_2OH$ solution to drive $Ag(NH_3)_2^+$ adsorbed on the surface of paper. Silver mirror reaction happened and Ag NPs generated when formaldehyde solution, a common reducing agent, was added. The reaction mechanism of the silver mirror reaction process can be expressed as

$$HCHO + 4[Ag(NH_3)_2]OH = 4Ag + 6NH_3 + (NH_4)_2CO_3 + 2H_2O$$

Two processes are involved in preparing paper substrate: adsorption of metal ions onto paper matrix and reduction of metal ions by chemical reduction to Ag NPs. the possible adsorption interactions between $Ag(NH_3)_2^+$ and filter paper is shown in Fig. 1B. It is well known that filter paper is made up of amounts of cellulose fibers with a mass of hydroxyl groups, showing negative surface charge. The immersion of filter paper into $Ag(NH_3)_2OH$ solution allows the adsorption of $Ag(NH_3)_2^+$ onto paper matrix through electrostatic attraction between $Ag(NH_3)_2^+$ and electronegative hydroxyl groups. Meanwhile, capillary attraction may also plays an important role in the adsorption process due to the existence of plenties of pores on cellulose matrix. $Ag(NH_3)_2^+$ is then reduced by formaldehyde to form Ag atom. The addition of $NH_3 \cdot H_2O$ to $AgNO_3$ solution lowers the redox potential from $+0.7991$ V (Ag^+/Ag^0) to $+0.373$ V($[Ag(NH_3)_2]^+/Ag^0$) by the formation of chelates, thus limiting the rate of nucleation [34]. This results in the formation of preferred uniform silver nuclei on cellulose fibre, which serve as seeds for the subsequent growth process. As a result of positive surface charge of formaldehyde-reduced Ag NPs, they have electrostatic attraction to cellulose fibre with electronegative hydroxyl groups, sticking to cellulose fibre more firmly. At the same time, Ag NPs with positive surface charge are repelled to avoid aggregation of Ag NPs, leading to the uniform distribution of Ag NPs on the paper matrix. In this way, we are able to fabricate Ag NPs on filter paper with high density size as SERS-active paper. The Ag NPs prepared by this in situ silver mirror reaction method stick to cellulose fibre more firmly, which will not be washed out by water or other solvents.

Photograph of prepared Ag NP-based filter paper is shown in Fig. 2. Ag NPs were decorated on a common filter paper with the diameter of 9 cm, and only 3 mm × 3 mm substrates are enough for the SERS experiments. At least 700 pieces of substrates can be acquired just from prepared Ag NP-based filter paper on account. That is to say, our Ag NP-based filter paper can be divided into many blocks and SERS experiments can be carried out on many occasions for a piece of Ag NP-based filter paper. In addition, the simple preparation method of paper substrate results in the possibility of mass production for the Ag NP-based paper. The Ag NP-based filter paper displayed a clear green-brown, indicating that Ag NPs were successfully deposited on the common

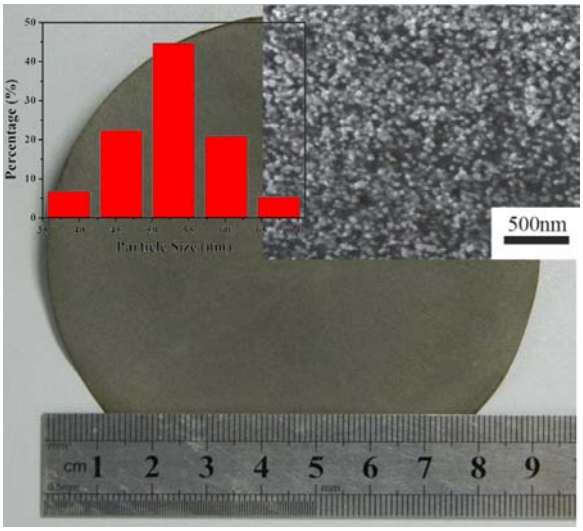

Fig. 2. Photograph of prepared Ag NP-decorated filter paper, insets show SEM image and particle size distribution of Ag NPs adsorbed on paper.

laboratory filter paper. Higher magnification image reveals Ag NPs with dozens of nanometers were densely decorated in a common filter paper. Insets also show the size distribution of Ag NPs. The size distribution of Ag NPs varies from 35 nm to about 72 nm with an average size of 53 nm, and the particle distribution was denser on paper which is suitable for SERS detection. SERS signals were collected by the portable Raman spectrometers with spot size of about 90 μm in diameter. In other words, several hundred thousands of Ag NPs were obtained in a spot range, which is beneficial to SERS test. On the basis of this result, the filter paper with dense Ag NPs can be used as practical SERS substrate.

3.2. SERS performance of the paper seRS substrates: sensitivity, reproducibility, stabilization

Herein, all SERS experiments were carried out with the assistance of 'D-SERS' method which owns very high detection sensitivity. First, to check for the influence of paper signals on our test, the SERS test of Ag NPs based filter paper was carried out. Some spectral features can be observed as one band located around 1000 cm^{-1} increased, which likely is caused by the C–O–C bending modes from cellulose fibre structures and adsorption of byproduct from the silver mirror reaction. Nevertheless, intensities of these peaks are too weak to have impact on the signals of analytes, which is confirmed when CV molecules are detected by the paper substrate. Substrate signals are barely observed with the existence of analytes molecules (Fig. S1).

In this investigation, two different experiments were devised. First, 10^{-8} M CV solution was dropwised onto paper substrate and 'D-SERS' spectra were collected during solvent evaporation process. Second, SERS signals were collected after absolute evaporation of 10^{-8} M CV solution on paper substrate. From Fig. 3B, we can find that stronger SERS signals are apparently observed using 'D-SERS' method. Possible reasons are followings. First, the existence of solvent brings these analyte molecules into the matrix of paper substrate, increasing the chance of contact between Ag NPs and targets. Second, movement of analyte molecules intensifies enormously during the solvent evaporation process and the frequencies of molecules colliding with Ag NPs are increased accordingly to gain stronger signals. Besides, solvent evaporation is also a kind of concentration process, which can also cause the enhancement of SERS signals. That's why 'D-SERS' is an effective method for realizing highly sensitive detection.

Another advantage also drives us to choose 'D-SERS' technique to realize our portable detection. As we know, portable Raman system is absolutely necessary for real-world detection. However, a high laser power of the portable Raman system is too much for the dry state SERS substrate with long accumulation time. And it is true that it can easily melt nanoparticles as well as burns paper with long time exposure under high laser power. However, detection performance with 'D-SERS' method can avoid this weakness, because solvent can act as a protective agent, the existence of water can prevent the burning of filter paper. Simultaneously. oxidation of silver nanoparticles on substrates can be avoided under the laser irradiation because of the solvent protection [35].

We have discussed whether the Ag NPs loaded filter paper is suitable to serve as the SERS substrate. The first key element to a new SERS-active substrate is the sensitivity. To evaluate the SERS performance of the Ag coated paper substrate, we chose CV as probe molecular. Fig. 3 shows results of SERS spectra with different CV concentrations from 10^{-7} to 10^{-9} M on the paper substrate. Several main peaks of the CV molecules were exhibited here, the vibrational bands at 1619, 1585 cm^{-1} were attributed to the aromatic C–C stretching modes, an *N*-phenyl stretching mode corresponded to the peak at 1370 cm^{-1}, and bands at 1171, 915, and 809 cm^{-1} belonged to aromatic C–H bending modes [36–37]. From these results, one can observe that our Ag NPs-based filter paper substrate reveal excellent sensitivity and can indeed be used as a SERS substrate. As discussed above, D-SERS is one of reasons to acquire the splendid sensitivity. Moreover, particle size plays an important role in the SERS sensitivity and Ag NPs with sub-100 nm in diameter show the best SERS performance, the average size of the prepared Ag NPs by silver mirror reaction is about 53 nm which is in accordance with theoretical data.

To further assess the reproducibility of Ag NP-based substrates, the intensities of the main vibration of CV molecules from the 30 spots on the same substrate and 20 spots on the different batches SERS spectra are described (Fig. S2 and S3). The main Raman vibrations of CV molecules at 1173, 1370, 1620 cm^{-1} were obviously enhanced at all spots, indicating excellent SERS activity and reproducibility of our substrates. To get a statistically meaningful result, the relative standard deviation (RSD) of the Raman intensity of the carbon skeleton stretching modes was calculated [38]. Fig. S2 and S3 shows that our substrate demonstrates high reproducibility with less than 20% RSD of the major vibrations. We know that the paper largely consisted of microscale (~10 μm) cellulose fibrous strands interwoven together [22], which may affect the average distribution of Ag NPs on paper. Nevertheless, the portable Raman spectrometers with spot size of about 90 μm can eliminate this influence. The reason is that several cellulose fibrous strands can be observed in a spot range, and the average numbers of Ag NPs on cellulose fibres within a spot are similar, so SERS intensities vary in a small range and RSDs of the major vibrations are within 20%.

To evaluate the variation of the SERS signals caused by storage or aging, Raman experiments were conducted to detect CV molecules on account of its well-established vibrational features described above. A set of Ag NP-based filter paper were prepared

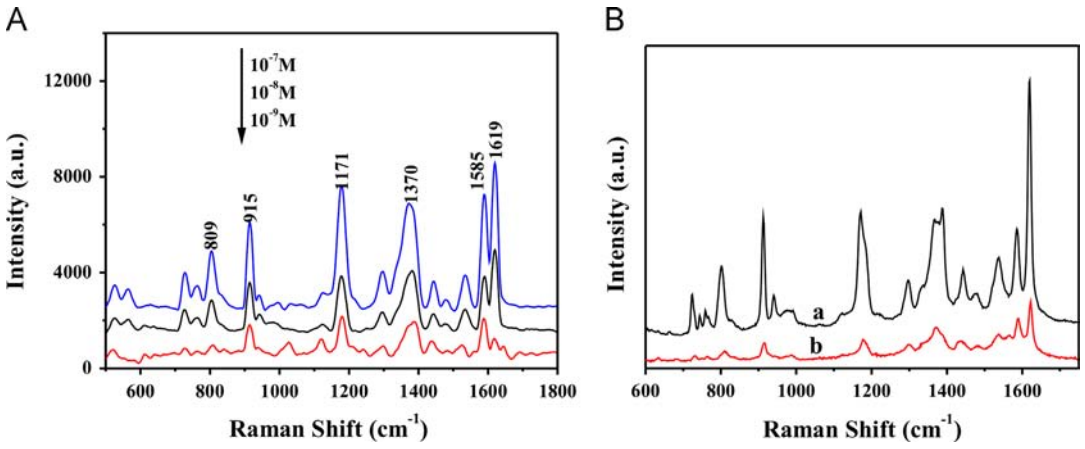

Fig. 3. (A) SERS spectra for Ag NP-based filter paper probed with the various concentrations of CV from10^{-7} to 10^{-9} M using 'D-SERS' method. (B) SERS spectra of 10^{-8} CV on filter paper substrate: (a) collected using 'D-SERS' method, (b) collected in the dry state.

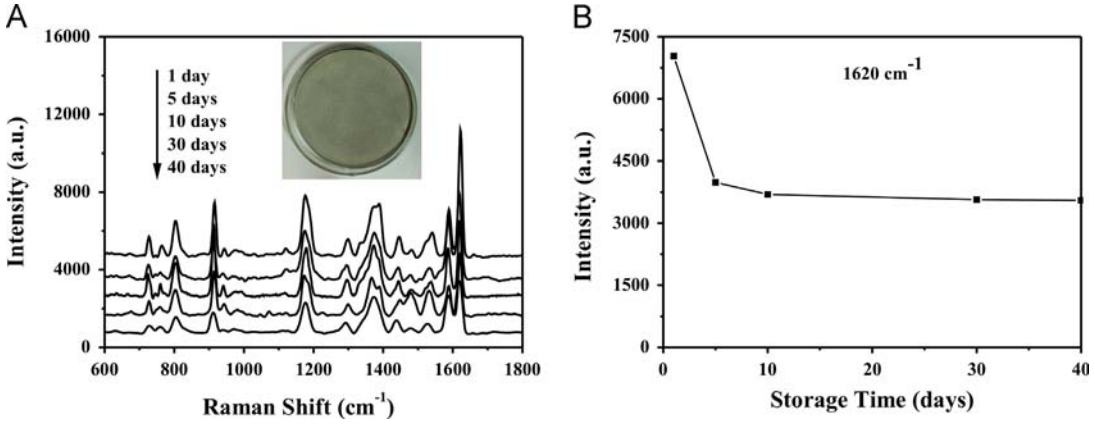

Fig. 4. (A) 'D-SERS' spectra of CV molecules by the enhancement of Ag NPs-based filter paper substrates with different storage time, insert shows the storage of paper substrate in a petri dish; (B) the corresponding SERS intensities at 1620 cm^{-1} as a function of reaction time.

and dried at room temperature prior storage. These substrates were kept in a petri dish at room temperature for different time without any special precautions (as Fig. 4A inset shown). After the designated storage the SERS experiments were conducted to obtain signals of CV on paper substrates. Fig. 4 shows the SERS spectra of CV molecules by the enhancement of Ag NP-decorated filter paper substrates with different storage time and the corresponding SERS intensities at 1620 cm^{-1} as a function of reaction time. The SERS signals decreased rapidly after stored for 5 days, and still cut down slowly until 10 days. However, the SERS signals didn't decrease further than half compared with the signals from freshly prepared substrates. The sensitivity compared to freshly prepared substrates is roughly a two-fold decrease in intensities.

To research this effect, XPS experiments were devised, characteristic bands of C. O and Ag were collected (Fig. S4). To quantitatively analyze the coverage of oxygen on the substrates during storage, band intensities of Ag3d5 (367.8 eV), C1s (286.2 eV) and O1s (532.2 eV) were calculated. Because cellulosic fiber in filter paper contributes to the signals of C1s and O1s, and only Ag elements were introduced to Ag NP-based substrate. The ratios of the band intensities of O1s to C1s are identical for filter paper and Ag NP-based paper substrate. The ratio value of O1s/C1s is 0.649 for freshly prepared substrates, whereas the ratio value increases to 0.701 for stored substrates. The change of ratio clearly indicates that the oxidation of Ag NPs happened rapidly after preparation of Ag NPs. For an accurate comparison, the surfaces of these substrates were further cleaned with HNO_3 solution to remove Ag_2O. After treatment of HNO_3 solution, nanoparticles decorated on the filter paper can still be observed, further confirming that Ag NPs didn't oxide actually. These results indicated that the oxidation of Ag NPs happened rapidly after preparation of Ag NPs, and the formation of oxide coating protects from Ag NPs further oxidization, thus substrates become stable for longer storage times. Compared to the other substrates which are conserved in water or other solvent to prevent the oxidization and keep the original sensitivity, our paper substrate exhibits convenient storage in the air without any treatment. More importantly, the decrease in detection intensities does not have much impact on the detection sensitivity.

3.3. *Detection of pesticide residues collected from various peels*

Pesticide residues are annually used in several million tons in agriculture and have caused intense public concerns by directly threatening human/animal's health due to their residues in agricultural products [39]. For instance, thiram, as a kind of pesticides, has been widely used as protective fungicides on field crops, tea, vegetables, and fruits and has harm to our skin and mucous membranes [40]. Therefore, SERS detection of pesticide residues in the real world is extremely urgent. In fact, the majority of SERS substrates are confined to laboratory research and many limits hinder the practical application of lab-based SERS substrate. Ag NP-decorated filter paper, because of its low cost, portability, flexibility and high efficiency of collecting sample with the high sensitivity and reproducibility, meet the demands for practical SERS substrates and can be used in solving critical problems for pesticide residues in the real world.

One of the distinct advantages of the paper-based SERS substrate is acting as a rag and has the ability to collect trace amount of analytes from real-world surfaces by swabbing across the surface. Herein, we put the fabricated paper substrate into the identification and detection of pesticide residues at many peels. Fig. 5 illustrates the sample collection process at a peel and the principle to detect pesticide residues on paper rag with 'D-SERS' technique. In general, the pesticide residues both adsorb at the surface of fruit peels and permeate into the inner of peels. Meanwhile, most of fruit peels have a rough surface with high amplification, which will cut down the collection efficiency of pesticide molecules from peel matrix. That's why efficiency of the sample collection is a decisive factor in real-world applications, a feature that is impossible with today's rigid SERS substrates. As mentioned above, residues can be loaded into the paper substrate by swabbing the inherently flexible device across a wide-area surface of fruit peels. In other words, rag paper substrate was employed to collect pesticide molecules from peel surfaces. Specifically, a droplet of mixture with ethanol and water is firstly added onto the peels and ethanol can disassociate the pesticide molecules from peel matrix, which is equal to a simple extraction to increase the analyte concentration at the outer surface of peels, while the existence of water prevent the fast evaporation of ethanol molecules and a piece of paper substrate was used as a rag to swab across the wide-area surface. Capillary attraction due to plenties of pores of cellulose matrix will cause the pesticide molecules into cellulose matrix with ethanol and water to make pesticide residues collected on the paper rag, as showed in Fig. 5A. SEM image of paper substrate after swabbing surfaces was shown in Fig. S5. Compared with SEM image of freshly prepared paper substrate, the size distribution of nanoparticles on filter paper didn't change after swabbing surfaces. In other words, swabbing across the surfaces didn't cause any change of both the filter paper and Ag NPs and didn't interfere the following detection and identification.

Despite of the high sample collection efficiency of rag paper, 'D-SERS' technique also plays a part due to forming plenty of hot spots and the volatilization-induced automatic concentration of the target molecule during the detection process. Combining rag paper substrate with 'D-SERS' method, sample collection efficiency and high detection sensitivity and reproducibility are realized, which is absolutely necessary for a practical substrate. The fingerprint information of pesticide molecules on the Ag NP-based paper substrate can be directly obtained from a portable Raman system during the evaporation process. Compared with the

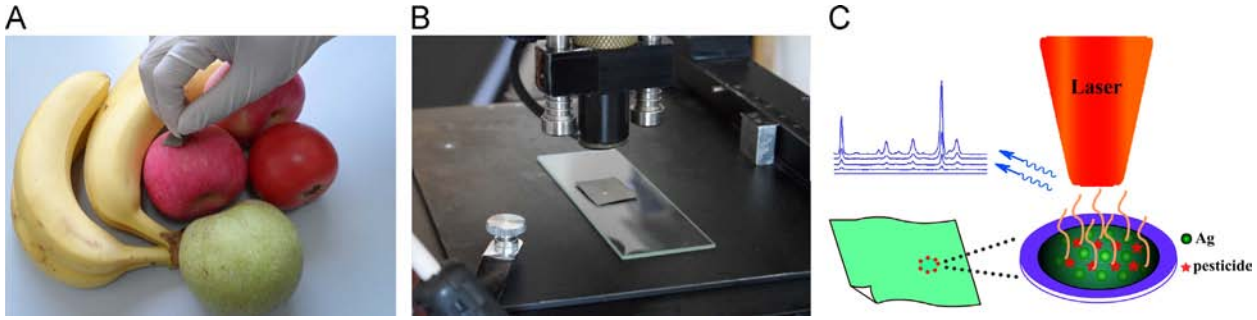

Fig. 5. (A) Sample collection process on a peel; (B) detection process with the portable Raman spectrometer; (C) schematic drawing for the detection of pesticide on paper rag with 'D-SERS' technique.

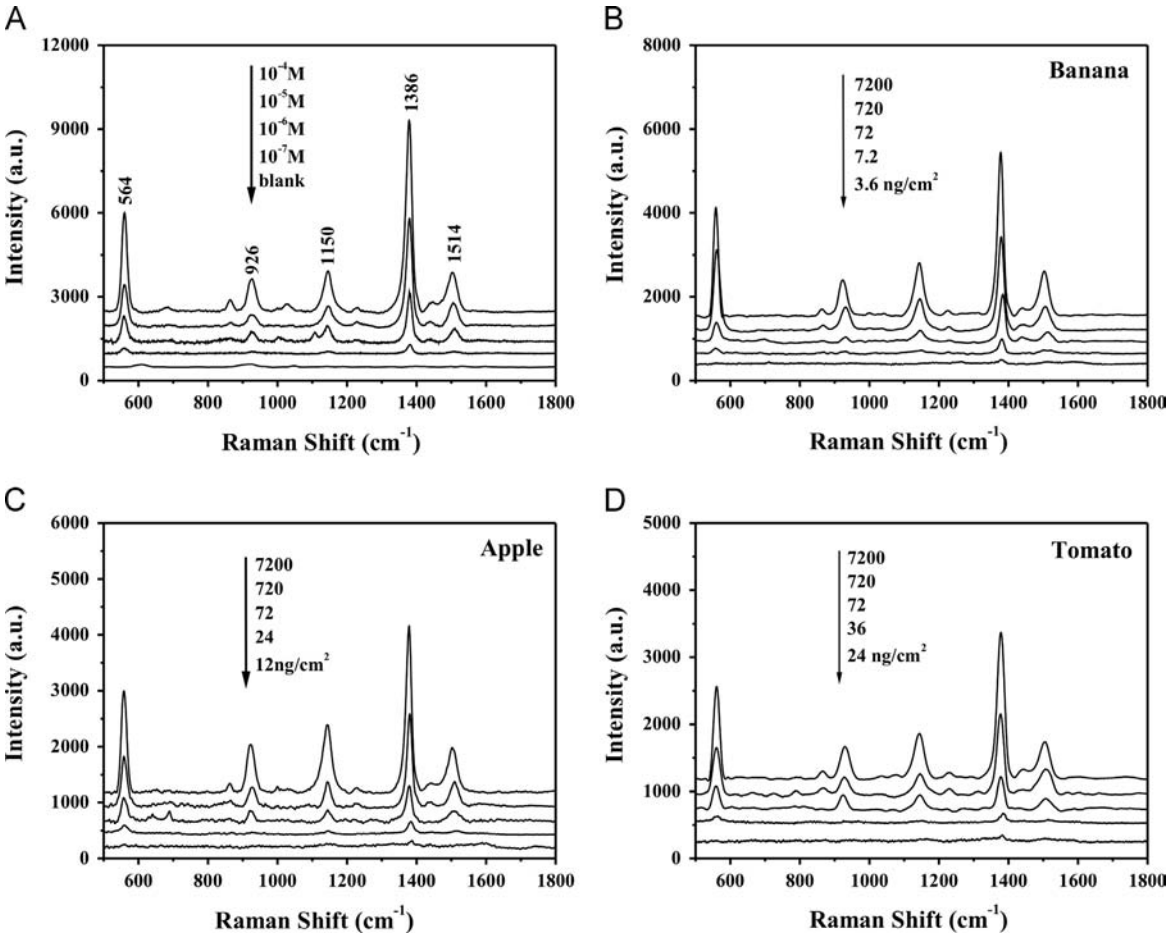

Fig. 6. 'D-SERS' spectra of thiram by the enhancement of Ag NP-based filter paper: (A) with different concentrations; and collected from the surfaces of (B) bananas; (C) apples; (D) tomatoes.

technique that nanostructures were added to the surface of fruit peels with pesticide residues, our way to put residues on the substrate eliminate the influence of fruit peels on SERS signals, because many fruits, such as apple and mango, have its own SERS signals which affect our detection.

SERS detection of thiram with different concentrations from 10^{-4} to 10^{-7} M was exhibited in Fig. 6A. The main Raman bands include 564 cm^{-1} attributed to υ (S–S), 1150 cm^{-1} to ρ (CH_3) or υ (C–N), and 1386 and 1514 cm^{-1} to ρ (CH_3) or υ (C–N), respectively [41]. From these results, our Ag NPs-based filter paper substrate revealed prominent sensitivity to thiram. The reason is formation of the resonated radical structure to thiram molecule easily when interacting with the metal surface, leading to the S–S bond cleavage of thiram, which give rise to two dimethyl residues that are strongly adsorbed onto Ag NPs [42]. The SERS technique for the detection of thiram residues at three different peels (banana, apple and tomato) was demonstrated in Fig. 6B–D. 10 μL thiram solution with different concentrations was added to the peels and completely dried at room temperature, thiram was then collected by mixture with ethanol and water onto paper substrate described above. The SERS signals were acquired from the substrate during the evaporation of thiram solution. Compared with Fig. 6A that thiram was detected after the thiram solution was directly added to the paper substrate, Fig. 6B displays an obvious decrease on the SERS sensitivity, the reason is that some pesticide molecules were penetrated into the fruit matrix and partly were losing during the collection process, in addition to the evaporation from the peels. Fig. 6 also shows that the Raman sensitivity varies at different peels. Thiram residues collected from bananas peel exhibit the strongest SERS signal intensity, and the detection limit is as low as 7.2 ng/cm^2, and only a band located at 1386 cm^{-1} with weak intensity emerge in 3.6 ng/cm^2 which is hardly distinguished in portable Raman system with low resolution definition. Whereas a clear drop in SERS intensity with the detection limit of 24 ng/cm^2 can be observed from the surface of apples and 36 ng/cm^2 from that of tomatoes, respectively. The experiments at different peels indicate that the Raman signal intensities from the same pesticide dosage at different peels are distinctive. The variations in sensitivity should be attributed to the differences in the surface properties of peels, such as its roughness and adsorbance performance.

Fig. 7 showed the linear calibration curve constructed by monitoring the intensity of the strong 1386 cm^{-1} spectral feature as a function of analyte concentration after different concentrations of thiram collected from different peels were detected. The monitored band at 1386 cm^{-1} is was chosen as the calibration band due to its strong intensity. As can been seen, intensities vs log [C] shows excellent linear relationship. The correlation coefficient R^2 is higher than 0.98 for each kind of fruits. The detection of thiram molecule proved the feasibility of paper substrate for quantitative analysis.

Limits of detection, limits of quantitation, the correlation coefficient R^2 for each calibration curve is calculated and shown in Table 1. The limits of quality are calculated and determined by substituting the minimum distinguishable signal to fit equation of the linear calibration curve [43–44]. The results indicated limit of quality is different between three kinds of fruits and similar to the limit of detection, which further confirms the practical application

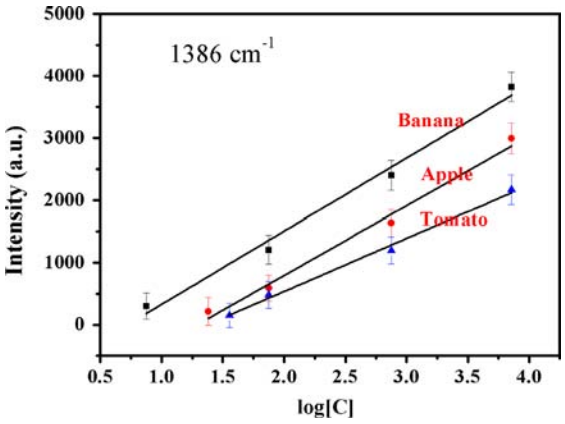

Fig. 7. Linear calibration curves constructed by monitoring the intensity of the strong 1386 cm^{-1} spectral feature as a function of analyte concentration after different concentrations of thiram collected from different peels were detected.

Table 1
Analytical figures of merit for the quantitative SERS detection of Thiram residues collected from three kinds of fruits.

Thiram residues at different peels	R^2	Limit of detection	Limit of quantitation
Banana	0.98522	7.2 ng/cm^2	7.8 ng/cm^2
Apple	0.98216	24 ng/cm^2	16 ng/cm^2
Tomato	0.99209	36 ng/cm^2	40.3 ng/cm^2

Table 2
The analytical features of the method.

Concentration	R^2	RSD
7.2 μg/cm^2	0.98216	12.9%

of paper devices in quantitative analytical fields, such as quantitative detection of food additives and other pesticides.

To further assess the reproducibility of Ag NP-based substrates for the practical detection of pesticide residues, the SERS intensity of the main vibration of thiram residues with the same concentrations were collected from 30 sets of apple peels by paper substrates (shown in Fig. S6). SERS intensities of thiram collected from different apples fluctuate in a small range, which further confirmed the high reproducibility of paper-based substrate.

The precision of the measurements was evaluated by above reproducibility of Ag NP-based substrates for the practical detection of pesticide residues. A relative standard deviations ($n=30$) was 12.9% at 1386 cm^{-1} with a concentration of 7.2 μg/cm^2. The analytical features of the method developed were summarized inTable 2.

To evaluate the stability of this method on real matrices, Raman experiments were conducted to detect thiram residues collected from apple peels by paper substrate with different storage times (shown in Fig. S7). From the results we can see, SERS signals of thiram residues collected from apple peels decreased rapidly at the primary 5 days and tended to stabilize after paper substrates were stored more than 10 days, which was in good accordance with the detection of standard samples. Meanwhile, the results verified the stability of this method on real matrices.

Similar results were inspecting paraoxon residues at various peels (Fig. S8). Although detection limits for different peels are all as low as 0.23 μg/cm^2, paraoxon residues collected from banana peel exhibit the strongest SERS signal intensity, and a clear drop in SERS intensity can be observed from the surface of apples and tomatoes. Compared with thiram, SERS signals of paraoxon showed lower intensity, the possible reason is weak interaction between paraoxon molecules and Ag NPs, because double bond in paraoxon molecule is hard to be destroyed to form Ag–S bond.

4. Conclusions

In summary, D-SERS substrate based on Ag NP-based common laboratory filter paper was successfully fabricated via simple silver mirror reaction at room temperature. In addition to the properties of the low cost, simple preparation, mass production, the paper substrate acts as a rag and possesses high sample collection efficiency by simply swabbing across the real-world surfaces. 'D-SERS' method was combined with paper substrates because of its high sensitivity and reproducibility. Ag NP-based paper substrates combined with 'D-SERS' method reveals highly SERS performance to CV molecules with detection range from 10^{-7} to 10^{-9} M and reproducibility with less than 20% RSD from different spots on the same substrate and the different batches. Roughly a two-fold decrease of SERS signals after long-time storage shows the favorable stability. More importantly, prominent detection performance were demonstrated when the Ag NP-based filter paper was used in detecting thiram and paraoxon residues at different peels, with the detection limit of 7.2 ng/cm^2 and 0.23 μg/cm^2 respectively. All of these splendid properties used for the SERS substrates open up a new opportunity for Ag NP-based filter paper as practical SERS substrate for more analytes detection.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2014.04.066.

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