Polydopamine-assisted in situ growth of AgNPs on face masks for the detection of pesticide based on surface-enhanced Raman scattering spectroscopy

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Research Article

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Abstract

Thiram is used as a fungicide and insecticide in agriculture to prevent white rot and anthracnose, but it also produces certain pesticide residues that endanger human health. Polydopamine (PDA) is an adhesive polymer that functionalizes almost all chemical materials, having been inspired by the adhesive properties of catechol and amines in mussel adhesive protein. In this work, we have fabricated a highly sensitive face mask (FM)-based surface-enhanced Raman scattering (SERS) substrate by depositing silver nanoparticles (AgNPs), using a PDA layer as an interface to promote adhesion. Face masks are currently ubiquitous, and are simple and easy to obtain, and this approach can be regarded as waste utilization. FM/PDA/AgNPs can detect Nile Blue A (NBA) probe molecules at concentrations as low as 1.0×10^{-9} M, and permit measurements with sensitivity and uniformity. The Raman substrate can be used to swab the surface of fruit to detect thiram at concentrations as low as 1.0×10^{-7} M, and the reproducibility has been assessed. The simple utilization of this flexible SERS substrate holds promise for its practical application in the field of pesticide control.

1. Introduction

Research has proved that the molecular structures of pesticides determine their stability and persistence, and most of them are difficult to excrete from the human body through the digestive system. Pesticide residues in fruits and vegetables cause chronic poisoning and can induce many chronic diseases. Thiram is a representative dithiocarbamate (DTC) fungicide with a strong protective effect, which can control white rot and anthracnose in fruit. Thiram should be used rationally; if it is widely used with other DTC pesticides, it can elicit nervous system, endocrine-disrupting, and carcinogenic effects, raising concerns for human health [1]. Pesticide residues are very harmful, and even at trace levels can increase physical burden and even severely disrupt ecosystems [2, 3]. The development of strategies to monitor the application of pesticides is of primary importance.

At present, many methods are available for detecting thiram, including fluorimetry [4], colorimetry [5], high-performance liquid chromatography [6], electrochemical analysis, and spectrophotometry. Surface-enhanced Raman scattering spectroscopy is a detection method based on molecular vibrations that can be used for trace analysis [7, 11, 14, 15, 18, 23–25, 28]. Electromagnetic enhancement arising from the local surface plasmon resonance of neighboring precious metal particles [8] and chemical enhancement caused by metal nanostructures and electric charge are the main mechanisms of Raman enhancement. The applicability of SERS depends on the design and realization of suitable substrates. Traditional rigid SERS substrates [9, 10, 12] require a complex pretreatment process, are not amenable to non-invasive detection, and can no longer meet the needs of rapid detection of pesticides on site. Newly emerging flexible substrates, such as cellulose [17, 25, 29–31], polymer films [26, 27, 32–39, 43], and other flexible materials [13, 16, 40–42], can be formed into variable shapes. Most flexible substrates can be applied as swabs to detect pesticides [14–22, 29], but many methods are costly and complicated to operate.

Face masks have become more and more important part of daily life. Here, we have successfully prepared a PDA/AgNPs substrate on face masks. Dopamine self-polymerizes in an alkaline environment to form a PDA layer bearing a large number of phenolic hydroxyl and amino functional groups, which can bind silver ions. Furthermore, PDA has some reducing ability, and can reduce silver ions to silver nanoparticles. In deatail, we have employed SEM to characterize the morphology of the substrate, and XPS to analyze the elemental composition. The FM/PDA/AgNPs substrate displays high uniformity and sensitivity for the detection of NBA molecules. In addition, in order to verify its practical application and reproducibility on various curved surfaces, the FM/PDA/AgNPs substrate has been used to detect thiram residues on fruits. The results prove that the substrate can realize waste utilization, is characterized by a simple preparation method, low production cost, high sensitivity, high uniformity, and reproducibility, and provides a potential platform for efficient and flexible SERS sensors for use in biochemical identification.

2. Experimental

2.1 Materials

Dopamine hydrochloride, silver nitrate ($AgNO_3$), Tris-base, hydrochloric acid, and Nile blue A (NBA) were purchased from Energy Chemical Co., Ltd. (Anhui, China). Thiram was purchased from Aladdin Industrial Co. (Shanghai, China). Ethanol and acetone were purchased from Tianjin Yongda Chemical Reagent Co., Ltd. (Tianjin, China). Other chemicals were of analytical grade or high reagent grade. Face masks and fruits were purchased from a randomly selected local supermarket (Shenyang, China).

2.2 Preparation of PDA/AgNPs on face masks

A schematic diagram of the preparation of PDA/AgNPs on a face mask is shown in Fig. 1. The face mask was first ultrasonically cleaned with a sequence of ethanol, acetone, and deionized (DI) water in order to remove other substances that may have been present on its surface. It was then dried in an oven at 50 ℃. Subsequently, the clean face mask was dipped in Tris-HCl buffer solution containing dopamine (2 g/L) and placed in the dark for 24 h. Due to spontaneous oxidative polymerization, a PDA-modified face mask was obtained. Finally, the face mask was thoroughly washed with DI water and dried in a nitrogen atmosphere. The obtained composite material is denoted as FM/PDA. After gentle washing with ethanol, acetone, and DI water, the FM/PDA was dried in an oven at 50 ℃. In order to achieve uniform growth of AgNPs on its surface, the obtained FM/PDA substrate was placed in a fresh $[Ag(NH_3)_2]^+$ solution and stirred for 12 h at room temperature. Because of the adsorption and reducing ability of PDA molecules, especially towards Ag^+ ions, AgNPs were preferentially deposited on the FM/PDA surface. After several hours of reaction, uniform substrates were produced. The as-prepared substrates obtained after washing with DI water are denoted as FM/PDA/AgNPs.

2.3 Characterization

The morphological characteristics of FM/PDA/AgNPs were observed by means of a scanning electron microscope (SEM, JEOL, JSM-7400V, Japan) operated at an accelerating voltage of 5.0 kV. X-ray

photoelectron spectra (XPS) were recorded on a Thermo Scientific ESCALab XI + spectrometer (Thermo Fisher, USA). Raman spectra were collected at room temperature (20 °C) with a Renishaw 2000 Raman spectrometer (Renishaw plc, Wotton-under-Edge, UK) using an excitation source with λ = 532 nm. The band of a silicon wafer at 520 cm^{-1} was used to calibrate the spectrometer. SERS spectra were acquired through a 50× objective lens, and data were processed using LabSpec software.

2.4 SERS performance test

To evaluate the sensitivity of the FM/PDA/AgNPs substrate, an ethanolic solution of NBA was diluted from 10^{-3} M to 10^{-9} M. Aliquots (2 μL) of ethanolic NBA solutions of different concentrations were dropped on the substrate and allowed to dry naturally.

2.5 Direct detection of pesticide residues

Fruits were thoroughly washed with DI water. Aliquots (10 μL) of ethanolic thiram solutions at concentrations ranging from 10^{-3} m to 10^{-7} m were then sprayed thereon and allowed to dry naturally. The spraying area was restricted to 1 × 1 cm^2. Then, the FM/PDA/AgNPs substrate was used to carefully swab the thiram on the surface of the fruit.

3. Results And Discussion

3.1 Morphological characterization

SEM images were acquired to inspect the morphology of the face mask at different magnifications, as shown in Fig. 2a, b. When the substrate was modified by dopamine, its original smooth and flat surface became rough and uneven, indicating successful self-polymerization of the dopamine (Fig. 2c, d). Figure 2e, f show SEM images of FM/PDA/AgNPs. It can be seen that AgNPs were uniformly distributed on the surface of the PDA-modified face mask, resulting in a large number of nanostructures and nano gaps, forming a large number of SERS hot spots.

3.2 Elemental and structural analysis

XPS was used to analyze the elemental composition and valence state changes according to the positions of the characteristic lines in the energy spectrum. As can be seen in Fig. 3a, the wide-scan XPS pattern of the original face mask features two peaks due to C and O, whereas that of the FM/PDA/AgNPs substrate (Fig. 3b) features four peaks due to C, O, N, and Ag, indicating successful assembly of the substrate. In Fig. 3c, the N 1s signal at 400 eV can be attributed to the NH_2 and NH groups in PDA [44]. The high-resolution XPS pattern of Ag 3d (Fig. 3d) features Ag $3d^{5/2}$ and Ag $3d^{3/2}$ signals at binding energies of 368.2 eV and 374.2 eV, respectively. Additionally, the splitting of the 3d doublet is 6.0 eV, indicating the presence of the Ag^0 state in FM/PDA/AgNPs [45].

3.3 SERS performance

The SERS performance of the FM/PDA/AgNPs substrate was evaluated using NBA as a probe molecule. Figure 4a shows the SERS spectra of NBA adsorbed on the substrate at a series of concentrations (10^{-3}–10^{-9} M). When the concentration was as low as 10^{-9} M, the SERS intensity (at 591 cm^{-1} for NBA) could still be clearly discerned [22]. This high sensitivity can probably be ascribed to effective hot spots on the FM/PDA/AgNPs substrate. Figure 4b shows the relationship between SERS intensity at 591 cm^{-1} and the logarithm of NBA concentration. The linear correlation coefficient is 0.990, which holds promise for accurate quantification of research targets. To examine the uniformity of the FM/PDA/AgNPs substrate, 16 random locations were selected for the recording of SERS signals from NBA, as shown in Fig. 4c. The %RSD of the peak intensity at 591 cm^{-1} within one FM/PDA/AgNPs substrate was 14.12% (Fig. 4d), indicating acceptable homogeneity.

3.4 Application in on-site detection

Swabbing is considered to be the most versatile sampling method, as it can be used to analyze target molecules from surfaces of various shapes [14–22, 29]. Therefore, the FM/PDA/AgNPs substrate was used to detect thiram residues on the surfaces of grapes and pears. Aliquots (10 μL) of ethanolic thiram solutions of different concentrations were sprayed on the surfaces of the fruit and allowed to dry naturally in air. The substrate was then swabbed on the target surface. As the concentration of thiram was increased, its characteristic peaks could be easily observed. As shown in Fig. 5a, b, Raman bands at 568 cm^{-1} (S – S stretching), 1145 cm^{-1} (S – C–N stretching, CH_3 rocking), and 1390 cm^{-1} (C – N stretching, CH_3 rocking) were clearly apparent in the spectra. The 1390 cm^{-1} peak could be used as an analytical readout to assay the residues on the surfaces of grapes and pears, as has been reported previously [46]. With decreasing thiram concentration, the SERS intensity of the characteristic peak decreased accordingly. Nevertheless, even when the thiram concentration was as low as 10^{-7} m, its characteristic peaks could still be observed. Figure 5c, d show that the SERS peak intensity (measured at 1390 cm^{-1}) conformed to a linear dependence on the concentration of thiram, which is the basis for quantitative spectral analysis. The results indicate reliable SERS quantification, with regression coefficients (R^2) of 0.988 and 0.910, respectively. By spraying an aliquot (10 μL) of a 1×10^{-7} m thiram pesticide solution on the surface of a grape, about 0.24 ng of thiram deposition can be estimated for an area of 1 × 1 cm^2, and the Raman intensities of the analyte at this level were recorded by the direct swabbing method. According to the above quantitative method, thiram residues on the surface of pears were likewise detected, and the detectable amount was as low as 0.48 ng/cm^2. The results show that the FM/PDA/AgNPs substrate has high SERS sensitivity, and that thiram residues can be detected on various surfaces.

To further explore the reproducibility of the FM/PDA/AgNPs substrate for the direct detection of pesticides on fruit surfaces, ten different grape surfaces bearing the same concentration of 2.40 ng/cm^2 were swabbed for residue determination. As shown in Fig. 6a, the characteristic band at 1390 cm^{-1} was consistently recorded. The Raman intensity fluctuations of thiram from the different grape surfaces were small, with a calculated RSD (n = 10) of 17.66% from the statistical results. This indicated that the

FM/PDA/AgNPs substrate had high reproducibility in practical analysis. These results make the FM/PDA/AgNPs substrate promising for practical applications.

4. Conclusions

In summary, inspired by an adhesive interaction in mussels, silver nanoparticles have been grown in situ on a polydopamine-modified face mask. In this way, an FM/PDA/AgNPs substrate with high sensitivity, uniformity, and reproducibility was obtained. Face masks are currently ubiquitous, and their further use can be regarded as waste utilization. The obtained substrate can be used to detect NBA probe molecules at concentrations as low as 1.0×10^{-9} M. The flexible FM/PDA/AgNPs substrate could be used to detect different concentrations of thiram pesticide on the surface of fruits by swabbing. Swabbing of ten different fruits with the substrate demonstrated good reproducibility. The FM/PDA/AgNPs substrate is flexible, making it very suitable for sampling and testing real samples. In addition, the simple preparation method can meet the growing demand for actual analysis and endows the substrate with great potential in the fields of environmental and biological sciences.

Declarations

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Competing Interests

The authors have no relevant financial or non–financial interests to disclose.

Ethics approval

Not applicable.

Consent to participate

Not applicable.

Consent for publication

Not applicable.

Availability of data and material

All data generated or analysed during this study are included in this published article.

Code availability

Not applicable.

Authors' Contributions

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Tongtong Wang, Qijia Zhang, Jia Li, Guangda Xu, Na Guo, Peng Song and Lixin Xia. The first draft of the manuscript was written by Tongtong Wang and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Figures

Figure 1

Schematic representation of the preparation process and utilization of FM/PDA/AgNPs.

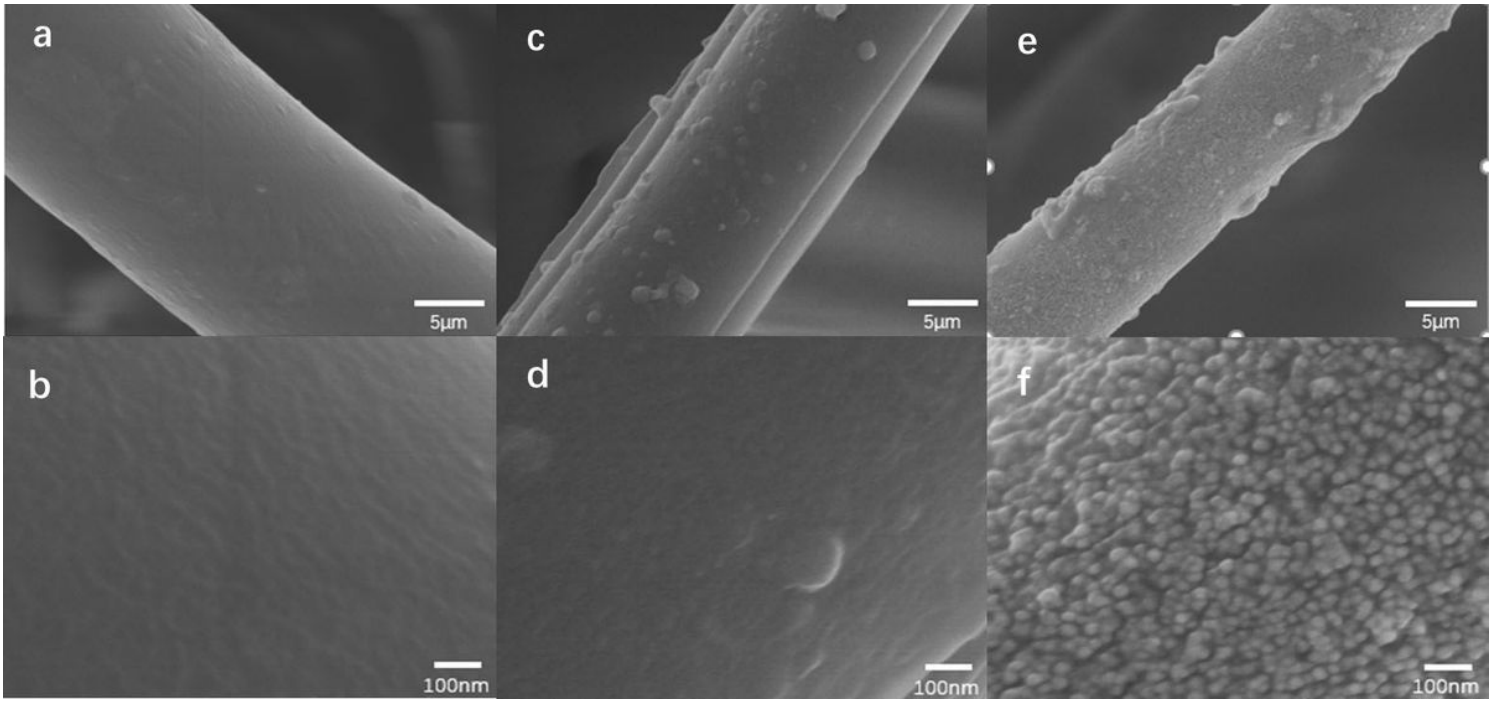

Figure 2

SEM images of (a, b) the original face mask, (c, d) FM/PDA, and (e, f) the FM/PDA/AgNPs substrate.

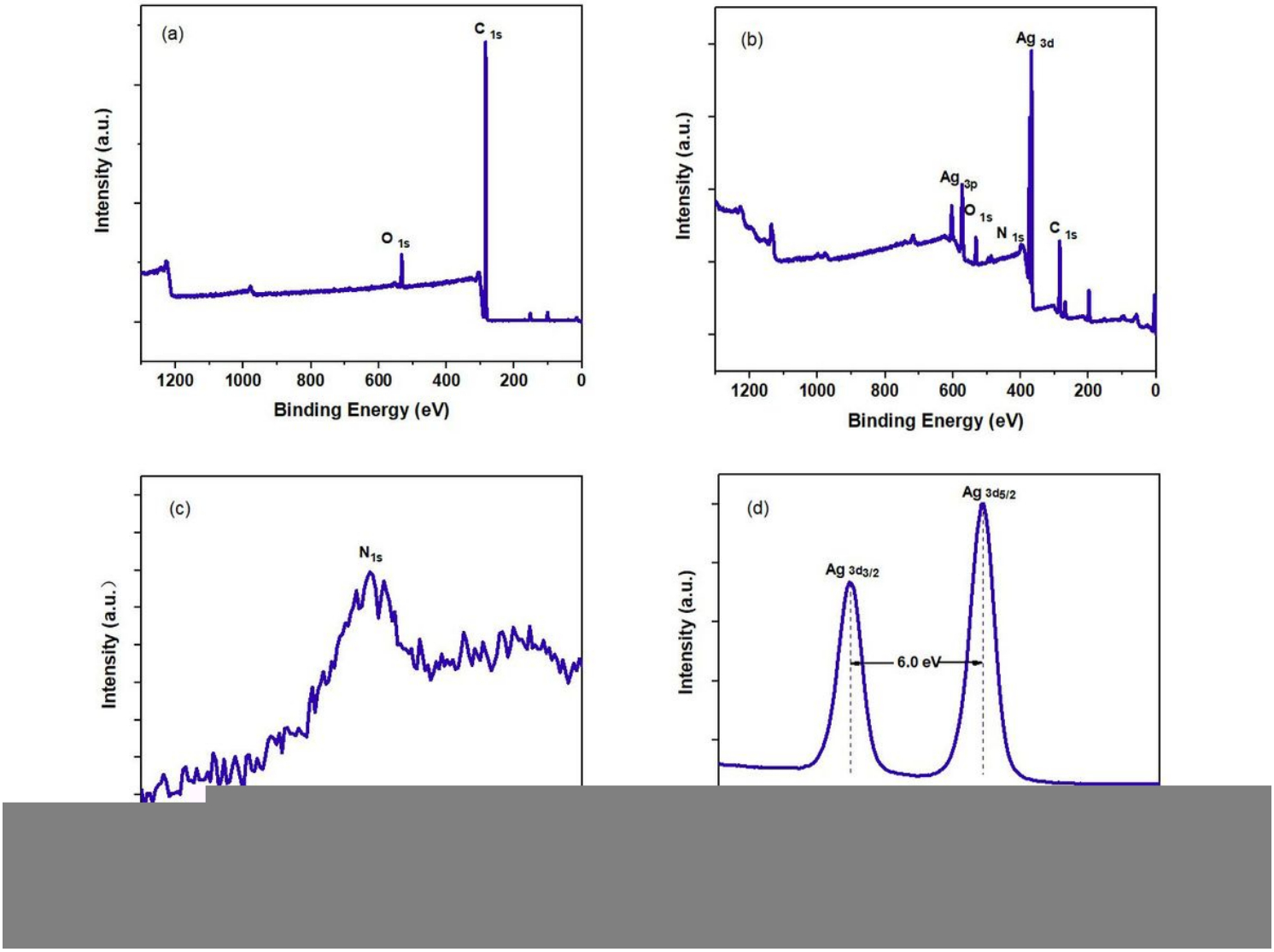

Figure 3

XPS patterns of (a) the original face mask, (b) the FM/PDA/AgNPs substrate, (c) N 1s, and (d) Ag 3d.

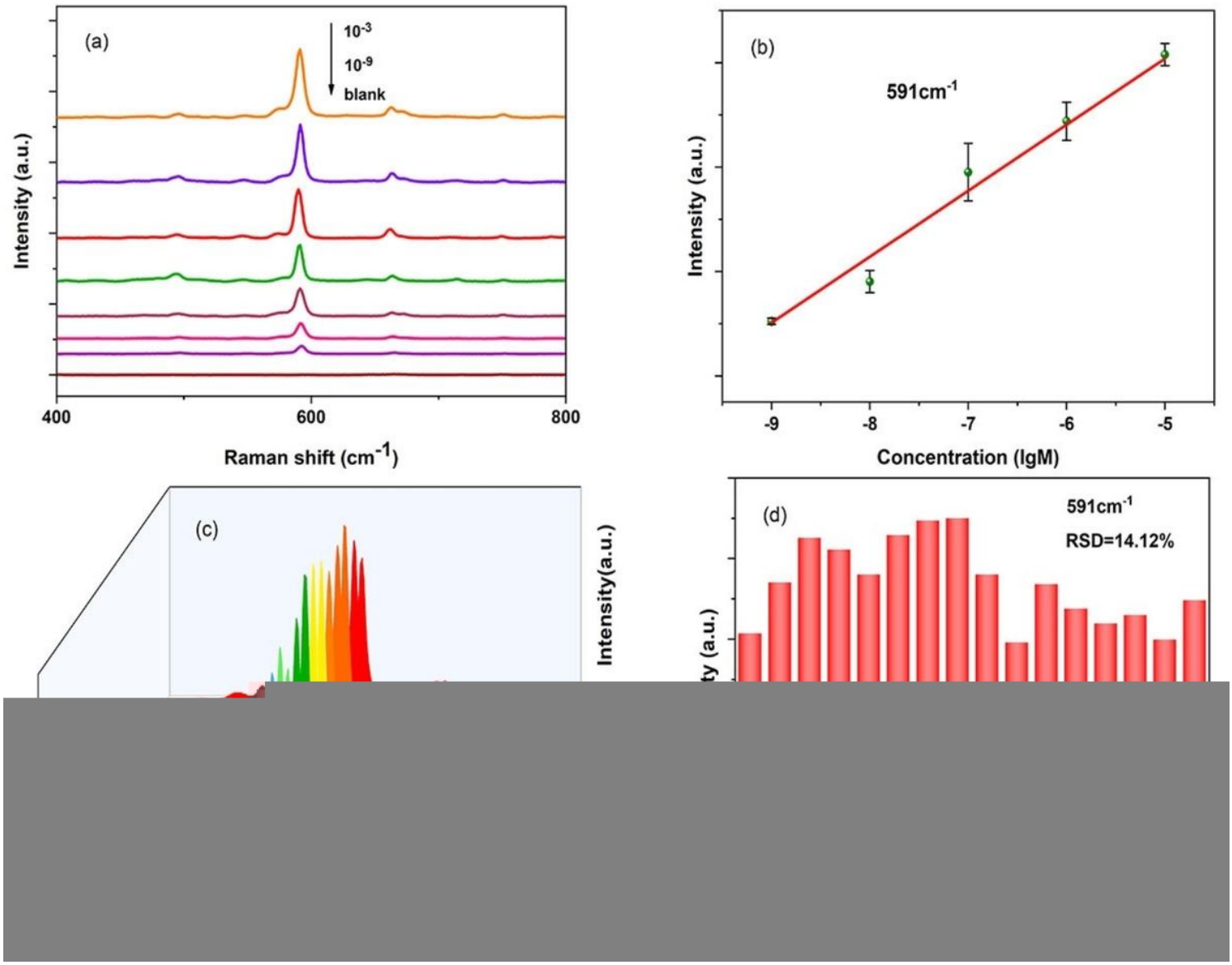

Figure 4

(a) Raman spectra of NBA deposited at 10^{-3}–10^{-9} m. (b) Relationship between the NBA signal intensity at 591 cm^{-1} and the corresponding logarithmic concentration. (c) SERS homogeneity of the FM/PDA/AgNPs substrate demonstrated by spectra acquired at 16 randomly selected points. (d) Raman intensity distribution of the NBA signal at 591 cm^{-1} collected from the 16 randomly selected points.

Figure 5

SERS spectra of thiram at different concentrations collected by FM/PDA/AgNPs substrates through swabbing extraction on (a) grape surfaces, (b) pear surfaces. Relationships between the SERS peak intensity at 1390 cm^{-1} and the corresponding logarithmic concentration of thiram on (c) grape and (d) pear surfaces collected by swabbing extraction.

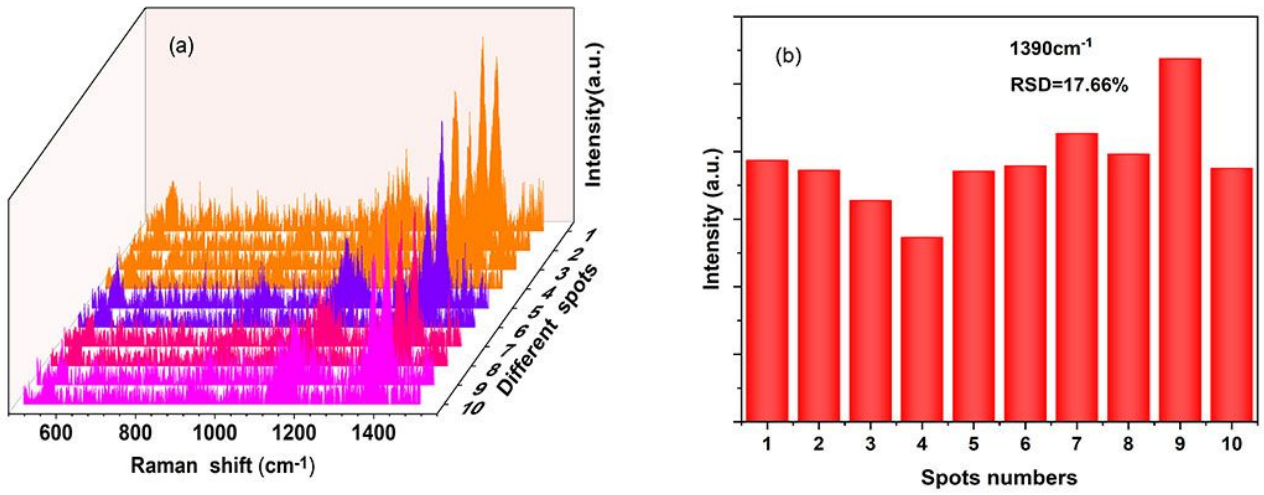

Figure 6

(a) Raman intensities of thiram sampled from ten different grapes using the FM/PDA/AgNPs substrate.
(b) Corresponding distribution of Raman intensities at 1390 cm^{-1}.