Polydopamine-Assisted In Situ Growth of AgNPs on Face Masks for the Detection of Pesticide Based on Surface-Enhanced Raman Scattering Spectroscopy

Tongtong Wang · Qijia Zhang · Jia Li · Guangda Xu · Na Guo · Peng Song · Lixin Xia

Received: 9 April 2022 / Accepted: 27 May 2022 / Published online: 6 June 2022
© The Author(s), under exclusive licence to Springer Science+Business Media, LLC, part of Springer Nature 2022

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 $1.0 \times 10^{-9}$ 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 $1.0 \times 10^{-7}$ 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.

Keywords Polydopamine · Face mask · Waste utilization · Flexible SERS substrate · Thiram

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 (SERS) 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 (FM) have become more and more important part of daily life. Here, we have successfully prepared a polydopamine (PDA)/silver nanoparticle (AgNPs) substrate on FM. 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. The FM/PDA/AgNP substrate displays high uniformity and sensitivity for the detection of Nile blue A (NBA) molecules. In addition, in order to verify its practical application and reproducibility on various curved surfaces, the FM/PDA/AgNP 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.

**Experimental**

**Materials**

Dopamine hydrochloride, silver nitrate (AgNO₃), Tris-base, hydrochloric acid, and 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. The FM (size 9.5 × 17 cm ± 10%; manufacturer Henan Yadu Industrial Co., Ltd.; composition non-woven fabric and polypropylene melted cloth) and fruit were purchased from a local supermarket (Shenyang, China). There were three layers after the FM had been cut, and the middle layer of polypropylene melted cloth was used.

**Preparation of PDA/AgNPs on FM**

A schematic diagram of the preparation of PDA/AgNPs on a FM is shown in Fig. 1. The FM 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 and to ensure that subsequent experimental operations were in a dust-free environment. It was then dried in an oven at 50 °C. Subsequently, the clean FM 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 FM was obtained. Finally, the FM 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 °C. In order to achieve uniform growth of AgNPs on its surface, the obtained FM/PDA substrate was placed in a fresh [Ag(NH₃)₂]⁺ solution and stirred for 12 h at room temperature. Because of the adsorption and reducing ability of PDA molecules, especially towards silver 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.

![XPS patterns](https://example.com/xps_patterns.png)

**Fig. 3** XPS patterns of a the original FM, b the FM/PDA/AgNPs substrate, c N 1 s, and d Ag 3d
Characterization

The morphological characteristics of FM/PDA/AgNPs were observed by means of a scanning electron microscope (SEM, JEOL, JSM–7400 V, 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.

SERS Performance Test

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

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 to 10⁻⁷ M were then sprayed thereon and allowed to dry naturally. The spraying area was restricted to 1 × 1 cm². Then, the FM/PDA/AgNP substrate was used to carefully swab the thiram on the surface of the fruit.

Fig. 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/AgNP 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.
Results and Discussion

Morphological Characterization

SEM images were acquired to inspect the morphology of the FM 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 shows SEM images of FM/PDA/AgNPs. It can be seen that AgNPs were uniformly distributed on the surface of the PDA-modified FM, resulting in a large number of nanostructures and nano gaps, forming a large number of SERS hot spots.

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 FM 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 1 s 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].
SERS Performance

The SERS performance of the FM/PDA/AgNP 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/AgNP 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/AgNP substrate, 16 random locations were selected for the recording of SERS signals from NBA, as shown in Fig. 4c. The relative standard deviation (RSD) of the peak intensity at 591 cm^{-1} within one FM/PDA/AgNP substrate was 14.12% (Fig. 4d), indicating acceptable homogeneity.

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/AgNP 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, CH₃ rocking), and 1390 cm^{-1} (C–N stretching, CH₃ 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 shows 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 cm², 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/cm². The results show that the FM/PDA/AgNP substrate has high SERS sensitivity, and that thiram residues can be detected on various surfaces.

To further explore the reproducibility of the FM/PDA/AgNP substrate for the direct detection of pesticides on fruit surfaces, ten different grape surfaces bearing the same concentration of 2.40 ng/cm² 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/AgNP substrate had high reproducibility in practical analysis. These results make the FM/PDA/AgNP substrate promising for practical applications.
Conclusions

In summary, inspired by an adhesive interaction in mussels, AgNPs have been grown in situ on a PDA-modified FM. In this way, an FM/PDA/AgNP substrate with high sensitivity, uniformity, and reproducibility was obtained. FM 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/AgNP 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/AgNP 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.

Author Contribution 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.

Funding This work was supported by the Special project of guiding local scientific and technological development by the central government of Liaoning Province (Grant No. 2022JH6/100100033), the National Natural Science Foundation of China (Grant No. 11974152 and 21671089), the Liaoning Province Natural Science Foundation of China (Grant No. 1088/1555-6611/ab881e), and the Liaoning Province Department of Education (LJKZ0097), and the Liaoning Provincial Natural Science Foundation of China (Grant No. 11974152 and 21671089), the Liaoning Province (Grant No. 2022JH6/100100033), the National Natural and technological development by the central government of Liaoning Province. 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/AgNP 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/AgNP 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.

Availability of Data and Material All data generated or analyzed during this study are included in this published article.

Declarations

Ethics Approval Not applicable.

Consent to Participate Not applicable.

Consent for Publication Not applicable.

Competing Interests The authors declare competing interests.

References

1. Xu X, Mathieu C, Berthelet J, Duval R, Bui LC, Busi F, Dupret JM, Rodrigues-Lima F (2017) Human arylamine N-acetyltransferase 1 is inhibited by the diethiocarbamate pesticide thiram. Mol Pharmacol 92:358–365. https://doi.org/10.1124/mol.117.108662
2. Nsibande SA, Forbes BPC (2016) Fluorescence detection of pesticides using quantum dot materials—a review. Anal Chim Acta 945:9–22. https://doi.org/10.1016/j.aca.2016.10.002
3. Oliveira MJ, Martin CS, Rubira RG, Batagin-Neto A, Constantino CJL, Aroca RF (2021) Surface-enhanced Raman scattering of thiram: quantitative and theoretical analyses. J Raman Spectrosc 83:3–8. https://doi.org/10.1002/jrs.6222
4. Mei H, Shu H, Lv M, Liu W, Wang X (2020) Fluorescent assay based onphenyl–modified g–CN4 nanosheets for determination of thiram. Microchim Acta 87:159. https://doi.org/10.1002/micr.20174
5. Kong L, Huang M, Chen J, Lin M (2020) In situ detection of thiram in fruits and vegetables by colorimetry/surface–enhanced Raman spectroscopy. Laser Phys 30:065602. https://doi.org/10.1088/1555-6611/ab881e
6. Liu S, Bai A, Zhou L, Yu C, Li Y, Fan S, Pan C (2015) Disipation and residues of thiram in potato and soil. J Chem 2015:623847. https://doi.org/10.1155/2015/623847
7. Kalachovy Y, Erzina M, Postnikov P, Svorcik V, Lyutakov O (2018) Flexible SERS substrate for portable Raman analysis of biosamples. Anal Surf Sci 458:95–99. https://doi.org/10.1016/j.apsusc.2018.07.073
8. Ding SY, Li JF, Ren B, Wu DY, Panneerselvam R, Tian ZQ (2016) Nanostructure–based plasmon–enhanced Raman spectroscopy for surface analysis of materials. Nat Rev Mater 1:16021. https://doi.org/10.1038/natrevmats.2016.21
9. Fan X, Hao Q, Li M, Zhang X, Yang X, Mei Y, Qiu T (2020) Hotspots on the move: active molecular enrichment by hierarchically structured micromotors for ultrasensitive SERS sensing. ACS Appl Mater Interfaces 25:28783–28791. https://doi.org/10.1021/acsami.0c05371
10. Hou X, Fan X, Wei P, Qiu T (2019) Planar transition metal oxides SERS chips: a general strategy. J Mater Chem C 7:11134–11141. https://doi.org/10.1039/c9tc03195b
11. Lin S, Lin X, Han S, Liu Y, Hasi W, Wang L (2020) Flexible fabrication of a paper–fluidic SERS sensor coated with a monolayer of core–shell nanospheres for reliable quantitative SERS measurements. Anal Chim Acta 1108:167–176. https://doi.org/10.1016/j.aca.2020.02.034
12. Machado TM, Peixoto LF, Andrade GFS, Silva MAP (2020) Copper nanoparticles–containing tellurite glasses: an efficient SERS substrate. Mater Chem Phys 278:125597. https://doi.org/10.1016/j.matchemphys.2021.125597
13. Ding Q, Kang Z, He X, Wang M, Lin M, Lin H, Yang DP (2019) Eggshell membrane–templated gold nanoparticles as a flexible SERS substrate for detection of thiabendazole. Microchim Acta 453:186. https://doi.org/10.1007/s00604-019-3543-1
14. Jalaja K, Bhuvaneswari S, Manjunatha G, Divyamol R, Anup S, Jobin C, Benny KG (2017) Effective SERS detection using a flexible wiping substrate based on electrospun polystyrene nanofibers. Anal Methods 9:3998–4003. https://doi.org/10.1039/c7ay00882a
15. Zhao H, Hasi W, Bao L, Liu Y, Han S, Lin D (2018) A silver self-assembled monolayer–decorated polydimethylsiloxane flexible substrate for in situ SERS detection of low–abundance molecules. J Raman Spectrosc 49:1469–1477. https://doi.org/10.1002/jrs.5418
16. Shi G, Wang M, Zhu Y, Wang Y, Ma W (2018) Synthesis of flexible and stable SERS substrate based on Au nanofilms/cicada wing array for rapid detection of pesticide residues. Opt Commun 425:49–57. https://doi.org/10.1016/j.optcom.2018.04.065
17. Song SW, Kim D, Kim J, You J, Kim HM (2021) Flexible nanocellulose–based SERS substrates for fast analysis of hazardous materials by spiral scanning. J Hazard Mater 414:125160. https://doi.org/10.1016/j.jhazmat.2021.125160
18. Nowicka C, Kowalska S, Kamińska, (2019) Flexible PET/ITO/Ag SERS platform for label–free detection of pesticides. Biosensors 9:111. https://doi.org/10.3390/bios9030111

19. Hoppemann EP, Yu WW, White IM (2013) Highly sensitive and flexible inket printed SERS sensors on paper. Methods 63:219–224. https://doi.org/10.1016/j.ymeth.2013.07.010

20. Wang Y, Jin Y, Xiao X, Zhang T, Yang H, Zhao Y, Wang J, Jiang K, Fan S, Li Q (2018) Flexible, transparent and highly sensitive SERS substrates with cross–nanoporous structures for fast on–site detection. Nanoscale 10:15195–15204. https://doi.org/10.1039/c8nr01628a

21. Picotti AL, Rizzato ML, Lusi AR, Romano RM (2022) Stamp–like flexible SERS substrate for in–situ rapid detection of thiram residues in fruits and vegetables. Food Chem 373:131570. https://doi.org/10.1016/j.foodchem.2021.131570

22. Wang C, Wong KW, Wang Q, Zhou Y, Tang C, Fan M, Mei J, Lau WM (2019) Silver–nanoparticles–loaded chitosan foam as a flexible SERS substrate for active collecting analytes from both solid surface and solution. Talanta 191:241–247. https://doi.org/10.1016/j.talanta.2018.08.067

23. Barbillon G, Graniel O, Bechelany M (2021) Assembled Au/ZnO nano–urchins for SERS sensing of the pesticide thiram. Nanomaterials 11:2174. https://doi.org/10.3390/nano11092174

24. Zhang Y, Zhu A, Wang Y, Zhang X (2021) Plasmonic structure with nanocavity cavities for SERS detection of pesticide thiram. Nanotechnology 32:135301. https://doi.org/10.1088/1361-6528/abd279

25. Agari S, Sun L, Lin J, Weng Z, Wu G, Zhang Y, Lin M (2020) Nanofibrillar cellulose/Au@Ag nanoparticle nanocomposite as a SERS substrate for detection of paraquat and thiram in lettuce. Microchim Acta 187:390. https://doi.org/10.1007/s00604-020-04358-9

26. Li L, Chin WS (2020) Rapid fabrication of a flexible and transparent Ag nanocubes@PDMS film as a SERS substrate with high performance. ACS Appl Mater Interfaces 12:37538–37548. https://doi.org/10.1021/acsami.0c01718

27. Pandey P, Vongphachanh S, Yoon J, Kim B, Choi CJ, Sohn JI, Hong WK (2021) Silver nanowire–network–film–coated soft substrates with wrinkled surfaces for use as stretchable surface enhanced Raman scattering sensors. J Alloy Compd 859:157862. https://doi.org/10.1016/j.jallcom.2020.157862

28. Liu X, Ma J, Jiang P, Shen J, Wang R, Wang Y, Tu G (2020) Large–scale flexible surface–enhanced raman scattering (SERS) sensors with high stability and signal homogeneity. ACS Appl Mater Interfaces 12:45332–45341. https://doi.org/10.1021/acsami.0c13691

29. Kwon G, Kim J, Kim D, Ko Y, Yamauchi Y, Yoo J (2019) Nanoporouscellulose paper–based SERS platform for multiplex detection of hazardous pesticides. Cellulose 26:4935–4944. https://doi.org/10.1007/s10570-019-02427-8

30. Xiong Z, Chen X, Liou P, Lin M (2017) Development of nanofibrillated cellulose coated with gold nanoparticles for measurements of melanine by SERS. Cellulose 24:2801–2811. https://doi.org/10.1007/s10570-017-1297-7

31. Liou P, Nagyizicki FX, Kong F, Mustapha A, Lin M (2017) Cellulose nanofibers coated with silver nanoparticles as a SERS platform for detection of pesticides in apples. Carbohydr Polym 157:643–650. https://doi.org/10.1016/j.carbpol.2016.10.031

32. Repetto D, Giordano MC, Foti A, Gucciardi PG, Mennucci C, Mongeot FB (2018) SERS amplification by ultra–dense plasmonic arrays on self–organized PDMS templates. Appl Surf Sci 446:83–91. https://doi.org/10.1016/j.apsusc.2018.02.163

33. Alyami A, Quinn AJ, Iacopino D (2019) Flexible and transparent surface enhanced Raman scattering (SERS)–active Ag NPs/PDMS composites for in–situ detection of food contaminants. Talanta 201:58–64. https://doi.org/10.1016/j.talanta.2019.03.115

34. Zhang J, Yan Y, Miao P, Cai J (2017) Fabrication of gold–coated PDMS surfaces with arrayed triangular micro/nanopyramids for use as SERS substrates. Beilstein J Nanotechnol 8:271–2282. https://doi.org/10.3762/bjnano.8.227

35. Zhu Y, Wu L, Yan H, Lu Z, Yin W, Han H (2020) Enzyme induced molecularly imprinted polymer on SERS substrate for ultrasensitive detection of patulin. Anal Chim Acta 1101:111–119. https://doi.org/10.1016/j.aca.2019.12.030

36. Chen D, Zhang L, Ning P, Yuan H, Zhang Y, Zhang M, Fu T, He X (2021) In–situ growth of gold nanoparticles on electropun flexible multilayered PVDF nanofibers for SERS sensing of molecules and bacteria. Nano Res 14:4885–4893. https://doi.org/10.1007/s12274-021-3530-9

37. Sun J, Zhang Z, Liu C, Dai X, Zhou W, Jiang K, Zhang T, Yin J, Gao J, Yin H, Li H (2021) Continuous in situ portable SERS analysis of pollutants in water and air by a highly sensitive gold nanoparticle–decorated PVDF substrate. Anal Bioanal Chem 413:5469–5482. https://doi.org/10.1007/s00216-021-03531-0

38. Liu R, Tang J, Yang H, Jin W, Liu M, Liu S, Hu J (2019) In situ decoration of plasmonic silver nanoparticles on poly (vinylidene fluoride) membrane for versatile SERS detection. New J Chem 43:6965–6972. https://doi.org/10.1039/c9nj00439d

39. Kumar P, Khosla R, Soni M, Deva D, Sharma SK (2017) A highly sensitive, flexible SERS sensor for malachite green detection based on Ag decorated microstructured PDMS substrate fabricated from Tarot leaf as template. Sens Actuators B chem 246:477–486. https://doi.org/10.1016/j.snb.2017.01.202

40. Liu J, Si T, Zhang L, Zhang Z (2019) Mussel-inspired fabrication of SERS swabs for highly sensitive and conformal rapid detection of thiram bactericides. Nanomaterials 9:1331. https://doi.org/10.3390/nano9091331

41. Zhou X, Li H, Yu G, Chen Y, Wang Y, Zeng Z, Chi L (2021) A highly–efficient, stable, and flexible Kapton tape–based SERS chip. Mater Chem Front 5:6471–6475. https://doi.org/10.1039/d1qcm00547b

42. Huang WR, Yu CX, Lu YR, Muhammad H, Wang JL, Liu JW, Yu SH (2019) Mass-production of flexible and transparent Te-Au nylon SERS substrate with excellent mechanical stability. Nano Res 12:1483–1488. https://doi.org/10.1007/s12274-019-2422-8

43. Sun J, Gong L, Lu Y, Wang D, Gong Z, Fan M (2018) Dual functional PDMS sponge SERS substrate for the on-site detection of pesticides both on fruit surfaces and in juice. Analyst 143:2689–2695. https://doi.org/10.1039/c8an00476e

44. Ran J, Bi S, Jiang H, Telegin F, Bai X, Yang H, Cheng D, Cai G, Wang X (2019) Core–shell BiVO4@PDA composite photocatalysts on cotton fabrics for highly efficient photodegradation under visible light. Cellulose 26:6259–6273. https://doi.org/10.1007/s10570-019-02535-5

45. Gul SR, Khan M, Yi Z, Wu B, Fawad U (2017) Silver and molybdenum codoped TiO2: visible light active photocatalyst for photoelectrochemical applications. J Electron Mater 46:6440–6443. https://doi.org/10.1007/s11664-017-5666-7

46. Zhu J, Lin G, Wu M, Chen Z, Lu P, Wu W (2018) Large-scale fabrication of ultrasensitive and uniform surface–enhanced Raman scattering substrates for the trace detection of pesticides. Nanomater 8:520. https://doi.org/10.3390/nano8070520

Publisher’s Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.