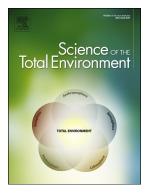
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### A review on nanomaterial-based SERS substrates for sustainable agriculture

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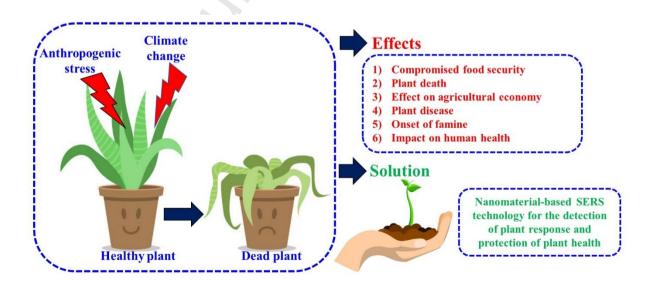
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# **Graphical abstract:**



**Abstract** The agricultural sector plays a pivotal role in driving the economy of many developing countries. Any dent in this economical structure may have a severe impact on a country's population. With rising climate change and increasing pollution, the agricultural sector is experiencing significant damage. Over time this cumulative damage will affect the integrity of food crops and create food security issues around the world. Therefore, an early warning system is needed to detect possible stress on food crops.

Here we present a review of the recent developments in nanomaterial-based Surface Enhanced Raman Spectroscopy (SERS) substrates which could be utilized to monitor agricultural crop responses to natural and anthropogenic stress. Initially, our review delves into diverse and costeffective strategies for fabricating SERS substrates, emphasizing their intelligent utilization across various agricultural scenarios. In the second phase of our review, we spotlight the specific application of SERS in addressing critical food security issues. By detecting nutrients, hormones, and effector molecules in plants, SERS provides valuable insights into plant health. Furthermore, our exploration extends to the detection of contaminants, chemicals, and foodborne pathogens within plants, showcasing the versatility of SERS in ensuring food safety. The cumulative knowledge derived from these discussions illustrates the transformative potential of SERS in bolstering the agricultural economy. By enhancing precision in nutrient management, monitoring plant health, and enabling rapid detection of harmful substances, SERS emerges as a pivotal tool in promoting sustainable and secure agricultural practices. Its integration into agricultural processes not only augments productivity but also establishes a robust defense against potential threats to crop yield and food quality. As SERS continues to evolve, its role in shaping the future of agriculture becomes increasingly pronounced, promising a paradigm shift in how we approach and address challenges in food production and safety.

**Keywords:** Nanomaterials; Surface Enhanced Raman Spectroscopy (SERS); Sustainable agriculture; Food Security; Plant Health

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### **1.0 Introduction**

Agriculture plays an important role for driving the economy of a country (Yaqoob et al., 2022). The economy of many developing countries is dependent on their agricultural products (Pallathadka et al., 2023). A healthy sustainable agricultural practice contributes towards the improvement of a regional economy and promotes healthy livelihood (Fahad et al., 2022). Thus, safeguarding agricultural product is important for preserving the economy of a country. Rapid industrialization and economic growth have led to increased anthropogenic stresses on the environment. Industrial activities, such as manufacturing, energy production and transportation often contribute to environmental degradation through various means, including pollution, deforestation, habitat destruction, and greenhouse gas emissions. These activities can have significant negative impacts on the environment, ecosystems, and natural resources. The agricultural sector is not exempt from these anthropogenic stresses. Intensive farming practices, excessive use of chemicals, deforestation for agricultural expansion, and water pollution from agricultural runoff can all contribute to environmental degradation (Choudhury et al., 2022). It is essential to address these issues and strive for sustainable practices in both agriculture and industry. Various organic and inorganic pollutants are accumulating in the ecosystem and eventually translocating into the plant system (Okoye et al., 2022). Contaminated plants are then consumed by humans and are essentially becoming part of our diet. Gradually these contaminants may accumulate in our body, causing disease (Yu et al., 2016). To mitigate this issue, it is vital that the scientific community and industry have the means to detect these types of anthropogenic stressors readily within our food products. The development of such a detection technique must meet certain criteria: rapid on-site screening of agricultural products, instant freshness check of vegetables and fruits, rapid detection of pesticides, antibiotics and formative additives inside different kinds of vegetables, meat and fruits, and quick detection of metals and organic pollutants in environmental samples including soil, water and plant systems. Traditional detection techniques such as mass spectrometry, chromatography and enzymelinked immunosorbent assay (ELISA) have the potential to accurately detect organic and inorganic contaminants in agricultural products as per national and international standards (Liu et al., 2022). But these techniques involve costly chemicals, sophisticated procedures and destruction of the analysed samples (Hussain et al., 2019). In addition, these procedures are often time consuming and may require a sophisticated preparatory process (Sohrabi et al., 2021). The analytical instruments are usually bulky and the maintenance costs are high. Operation of these instruments requires specialized persons with professional training (Liu et

al., 2022). Thus, researchers from around the world are striving to develop new approaches which could eliminate these complications and simplify the chemical analysis of contaminants in agricultural products, making the process much more feasible and rapid for the layperson.

With the development of artificial intelligence, groups of researchers are currently focusing on developing smart sensors which can improve the basic structure of an agricultural system and make it more intelligent (Gubbi et al., 2013). This development is on the verge of replacing laborious detection methods for contaminants and will make the overall process automated. Presently there are different types of sensors that are utilized in the agricultural sector which include sensors for measuring the physicochemical parameters of soil and water, pressure sensors, gas sensors, humidity sensors, photoelectric sensors and other sensors for monitoring food storage, crop harvest and pest control (El-Mesery et al., 2019; Siddiqui et al., 2014). These sensors mainly work on the basis of electrical current, chemiluminescence, fluorescence, electrochemical reactions and colour. These sensors perform well for the detection of specific parameters but suffer from drawbacks such as narrow spectrum of applicability and inaccuracies, which make them unfit for monitoring the quality of food (Damez and Clerjon, 2013). Therefore, it is necessary that a specific sensor must be developed with high efficiency and broad-spectrum applicability.

Surface-enhanced Raman Spectroscopy (SERS) is an emerging technology which can detect trace amount of analytes in a short interval of time and has an ultrasensitive detection level (Muchlethaler et al., 2016). The technique is very simple to use and has a high level of operational functionality. Principally, SERS works on the phenomenon of Raman spectroscopy which works on inelastic scattering of light and thus provides fingerprint like spectrum for certain analytes in accordance with its intensity and vibrational frequency (Wu et al., 2021). In recent years this specific property of SERS has been used in various segments of nanotechnological modules which are widespread across many scientific disciplines (Mousavi et al., 2022). The building block of nanotechnological modules are different kinds of nanoparticles (NPs) which have specific surface plasma resonance (SPR) which shows distinct plasmonic resonance during inelastic scattering process (Nilghaz et al., 2022; Plou et al., 2022). SERS works by two mechanisms, one is chemical enhancement where chemical analytes enhance the SERS signal, whereas the other is electromagnetic enhancement where SERS signals are enhanced by hot spots resulting from incorporation of nanostructured gold or silver nanoparticles (Moldovan et al., 2022; Sun, 2022). In electromagnetic enhancement SERS substrate enhances the local surface plasmon resonance and the Raman signals are greatly

enhanced by the nanomaterial present in the hot spot region (Luo et al., 2021; Yilmaz et al., 2022). This enhances the detection capability of spectrometric modules to the level of single molecule detection. The development of optimised SERS based substrates provides a very promising outlook for the analysis of contaminants in agricultural food crops (Gozdzialski et al., 2022; Hu et al., 2022; Liu et al., 2022). SERS has proven to be an effective tool for measuring contaminants in various food substances. However, currently there are no commercially available products that utilize SERS for detecting or quantifying contaminants inside food. Hence, in this review we present a broad discussion on the concept of SERS and the fabrication of various SERS substrates. Next, we focus on the application of SERS in different agricultural products and conclude with its impact on agricultural economy. Finally, we propose a future perspective on SERS technology which could be harnessed in various scientific avenues.

#### 2.0 Principle of SERS

Since its discovery, Raman spectroscopy (RS) has found its place in a variety of scientific endeavours, and is utilized in archaeology, medicine, materials, and food security due to low reagent consumption, high throughput, and rapid response time (Azbej et al., 2007; Breitman et al., 2007). The technique shows high specificity for the qualitative and quantitative analysis of molecular level structural backbone of different substances (Azbej et al., 2007). RS also offers other advantages such as high accuracy, simple sample pre-treatment procedures, and good reproducibility. However, it has a few drawbacks, for example the scattering light effect in RS is very weak and is  $1 \times 10^{-10}$  in comparison to that of incident light. Thus, detecting this small amount of light is problematic during real time analysis. Furthermore, the process lacks sensitivity and needs more time for the integration of incident light. This causes damage on the surface of the analytes. Certain modern Raman spectrophotometers have the ability to detect and analyse weak scattering light effectively. However, the spatial resolution of conventional Raman spectroscopy remains limited by the diffraction limit of light. As a result, it is challenging to obtain detailed information on small-scale features or analyse microstructures using this technique (Moldovan et al., 2022). To overcome these drawbacks conventional RS has been modified and SERS was introduced in the market (Mitchell et al., 2008). SERS works by enhancing the Raman scattering signal significantly when analyte molecules are adsorbed on the surface of a metal primarily made of nanoparticles or nanowires having nanoscale roughness. When RS is used to analyse these isolates on the nano surface it enhances the Raman

signal by 10<sup>14</sup>-10<sup>15</sup> fold which makes it possible for the detector to analyse trace amounts of substance at molecular level (Green and Liu, 2003; Kleinman et al., 2012).

The selection of the SERS substrate plays an important role in this type of spectrometric analysis. A good SERS substrate provides high reproducibility, good detection limits, low noise, high strength and high stability (Luo et al., 2021; Nilghaz et al., 2022; Plou et al., 2022; Sun, 2022). SERS employs rough metal surfaces or nanoparticles to confine materials in specific conglomerates, resulting in the modulation of the overall plasmonic resonance of the surface. Different surfaces have different activity and resonating potential which changes according to the shape and size of the nanoparticles. The SERS intensity also modulates as per their distance between the signalling molecule and the substrate and due to variation in the molecular spectrum.

As for a mechanistic insight into the SERS substrate, the performance of the SERS substrate depends on the chemical enhancement (CE) and electromagnetic enhancement (EE) of the SERS signal (Green and Liu, 2003; Kleinman et al., 2012). Electromagnetic enhancement is a physical effect which comes into play when local electromagnetic fields are enhanced due to plasmonic resonance of nanomaterial structure. EE is dependent on the distance between analytes and substrate. It is also non-selective in nature and offers a similar type of enhancement when analytes are placed in the hot spot. These hot spots are an agglomeration of the nanomaterial structure which enhances the Raman scattering. Maximum enhancement is achieved when analytes are located in the junction between two nanomaterial structures, whereas broadening occurs when they are in the peripheral region. High selectivity of the EE is observed at the junction, allowing for distinct peak resolution between two analytes. Chemical enhancement (CE) on the other hand is very selective in this criterion due to the specific interaction between substrate and the chemisorbed analyte molecules. The charge transferred during this interaction changes the polarizability of the molecule and allows the signal to amplify for proper detection (Schlücker, 2014; Yamamoto and Itoh, 2016).

The SERS signal, based on the residence of analytes and considering the detection modes, is divided into two categories: turned on and turned off. The on state occurs when analytes approach the SERS substrate, leading to an increase in the SERS signal. Conversely, the turn off state occurs when analyte molecules move away from the SERS substrate, resulting in a decrease in the SERS signal. SERS has distinct benefits when it comes to its usage in biosensing, as it is a non-invasive method of analysis. Additionally, SERS offers unique advantages in biosensing because it can provide a specific fingerprint of molecules,

conformation, and structure, and has the ability to detect multiple targets simultaneously due to the narrow width of Raman vibrational bands. In recent years, there have been advancements in Raman spectrometer technology, including miniaturization, making on-site SERS detection possible (Itoh et al., 2017; Panneerselvam et al., 2017). This is particularly important for field detection related to plants and animals, where a small and portable detection system is necessary. New technologies such as needle-tip enhanced Raman and confocal Raman have also emerged to improve sensitivity and spatial positioning (Cheng et al., 2014; Pang et al., 2016). This paper discusses the promising future of SERS detection for stress-related substances, which can be applied in the study of plant and animal stress resistance and inspire new research ideas for stress tolerance mechanisms through the development of substrates using new nanomaterials and combining SERS with other techniques (Cheng et al., 2014; Du et al., 2018). While some methods discussed may not be directly related to stress-related research, they can still provide insights into the application of SERS in this field.

### 3.0 Exploring Diverse SERS Substrates: Synthesis and Applications

Ultra-sensitive SERS sensors play a crucial role in various agricultural applications. The successful fabrication of diverse SERS substrates with nanomaterials/nanostructures is essential to achieve high sensitivity. These SERS substrates are categorised in **Fig 1** as per their usefulness for different agriculture purposes.

3.1 Fabrication of SERS substrate from colloidal nanoparticles

Colloidal noble metal nanoparticles, such as gold (Au) and silver (Ag), are commonly used as SERS substrates because they can generate hotspots upon aggregation, resulting in a strong enhancement of the Raman signal of the analyte molecules (Jeong et al., 2016). These nanoparticles can be functionalized or coated with different chemical species such as organic molecules, polymers, or silica shells to enhance their stability and SERS activity. The choice of materials and surface modifications can influence the chemical interactions between the analyte molecules and the SERS substrate, thereby affecting the SERS signal enhancement and sensitivity. The strong enhancement is due to the excitation of surface plasmons in the metal nanoparticles, which promotes the oscillation of electrons and generates localized electromagnetic fields that enhance the Raman scattering signal. There are different methods to prepare SERS substrates using colloidal noble metal nanoparticles, including photoreduction and chemical reduction methods (Langer et al., 2020). In the photoreduction method, a photosensitive reducing agent is used to reduce the metal precursor ions to form nanoparticles in the presence of a stabilizing agent. In the chemical reduction method, a reducing agent is

used to reduce the metal precursor ions to form nanoparticles in the presence of a stabilizing agent. The resulting SERS substrates can be either in the form of colloidal solutions or thin films on a substrate. The advantages of using colloidal noble metal nanoparticles as SERS substrates include the simple preparation procedure, low cost, easy storage, and strong enhancement ability. These properties make them suitable for a wide range of applications in SERS-based sensing, imaging, and detection. Colloidal nanoparticle-based SERS substrates (Fig 2) have been investigated in agriculture for decades, exemplified by Alak and Vo-Dinh's 1987 study utilizing silver-loaded microspheres to detect organophosphorus pesticides, critical for food safety (Alak and Vo-Dinh, 1987). These substrates offer high sensitivity and specificity in detecting pesticide residues in crops, soil, and water samples, mitigating health risks associated with pesticide exposure (Lu et al., 2018). Research has expanded into various agricultural applications, including mycotoxin detection in crops, monitoring pollutants, and identifying pathogens in livestock and crops (Jiang et al., 2018). The field has evolved rapidly, exploring nanomaterials of different shapes and sizes (Lu et al., 2018), tailored for specific chemical and physical properties to enhance contaminant detection efficacy. Nanomaterials can selectively bind to pesticides, antibiotics, or illegal additives, promising improved safety and quality of agricultural products (Arockia et al., 2015; Lu et al., 2014; Muhammad et al., 2020a; Yang et al., 2017; Yang et al., 2019b; Yang et al., 2016a; Yao and Huang, 2018a; Zhai et al., 2017; Zhou et al., 2020). Various SERS substrates (Table 1), such as silver  $\beta$ -cyclodextrin modified NPs (Qiu et al., 2022), Ag@SiO2 nanocubes (Mekonnen et al., 2018), and aptamermodified nanomaterials, demonstrate effectiveness in detecting specific contaminants in food products, showcasing nanotechnology's potential in agricultural safety and quality assurance (Jiang et al., 2019; Lu et al., 2014; Muhammad et al., 2020b; Qiu et al., 2022). Nanoparticles have several advantages for SERS analysis, but the aggregation of nanoparticles during measurements can cause significant variations in SERS activity and hinder quantitative and repeatable measurements. Aggregation can occur due to various factors, such as changes in temperature, pH, salt concentration, and surface chemistry. To overcome this issue, various approaches have been developed to control the aggregation of nanoparticles during SERS measurements. One approach is to modify the surface of nanoparticles with stabilizing agents, such as polymers, surfactants, or thiol-containing molecules. These agents can help to prevent the aggregation of nanoparticles and stabilize their colloidal dispersion in solution. Another approach is to immobilize the nanoparticles onto solid substrates, such as glass, silicon, or graphene, which can enhance the stability of the nanoparticles and reduce aggregation.

Furthermore, immobilization of nanoparticles onto solid substrates can provide a reproducible and well-defined SERS substrate, which can be used for quantitative and repeatable measurements. Regarding the adsorption capacity of target molecules to the nanoparticles, this can vary depending on the surface chemistry of the nanoparticles and the chemical properties of the target molecules (Yao and Huang, 2018b). To overcome this issue, functionalization of nanoparticles with specific targeting molecules, such as aptamers or antibodies, can be used to enhance the selectivity and sensitivity of SERS measurements for specific target molecules.

3.2 Nanostructured template-derived rigid SERS substrate

The utilization of nanostructured templates for fabricating SERS substrates (**Table 1**) presents several advantages compared to colloidal metal nanoparticles (Zhu et al., 2016). One significant benefit lies in the precise control afforded over the size and morphology of the substrate through the design and regulation of template morphology. These templates, crafted via techniques such as lithography, self-assembly, or electrospinning, from materials such as polymers, metals, or metal oxides, yield SERS substrates with well-defined morphological characteristics, including edge sharpness and gap size, enhancing SERS activity (Huang et al., 2013; Shen et al., 2014; Wali et al., 2019). Moreover, nanostructured templates ensure high uniformity and reproducibility in SERS substrates, crucial for quantitative and repeatable measurements. Achieving uniformity entails the control of fabrication parameters such as precursor solution concentration, reaction time, and temperature (Guselnikova et al., 2019; Muhammad et al., 2020a; Sun et al., 2016). This approach enhances substrate morphology control, reproducibility, and sensitivity in SERS measurements, though challenges with fragility and integration into practical systems persist, limiting their real-world applications (Muhammad et al., 2020b; Sun et al., 2016).

#### 3.3 Flexible SERS substrate

Flexible SERS substrates (Fig 3), fashioned from materials such as paper, tape, or polymer films and coated with metallic nanoparticles (Table 1), offer distinct advantages over rigid substrates such as glass or silicon (Ding et al., 2019; Huang et al., 2020; Parnsubsakul et al., 2020; Wang et al., 2018). These substrates are adaptable to diverse surfaces, lightweight, cost-effective, and conducive to on-site detection in complex environments (Hong et al., 2017; Ma et al., 2020; Wang et al., 2018). Moreover, their flexibility facilitates easy handling and storage, ideal for field applications (Chen et al., 2017; Chen et al., 2018; Lee et al., 2022; Li et al., 2018a; Wang et al., 2019a). Various materials, including adhesive tape, paper, natural biological material, and polymers, serve as platforms for SERS substrates. Paper-based substrates,

economically viable and efficient for trace pesticide detection, benefit from treatments including the application of alkyl alkene dimer to counter cellulose's hydrophilic nature (Lee et al., 2018). Adhesive tape, when combined with enhancing materials, becomes an effective substrate for "paste and peel" techniques, enabling efficient pesticide residue sampling from produce surfaces (Chen et al., 2016). Similarly, polymer-based substrates offer costeffectiveness, reproducibility, and flexibility, exemplified by modifications to hydrophilic polytetrafluoroethylene membranes with Au-NPs or transparent PDMS substrates with Au-NWs (Hong et al., 2017; Ma et al., 2020). Cotton cloth and chitosan find utility in SERS substrate fabrication, with in-situ synthesis of Ag-NPs on cloth or soaking chitosan sponge in Ag NPs suspension enhancing flexibility and detection capabilities (Chen et al., 2018; Wang et al., 2019b). Notably, Lee et al. (2022) demonstrated the flexibility and structural integrity of a SERS sensing platform using silver nanodendrites, even under substrate bending. However, challenges persist, notably fluorescence interference, emanating from samples or impurities, dampening sensitivity and accuracy (Chen et al., 2016). Additionally, low reproducibility in SERS measurements arises from substrate quality, stability, and signal-to-noise ratio variations (Gong et al., 2019). Overcoming these challenges is crucial for maximizing the potential of flexible SERS substrates in practical applications, expanding their utility in diverse fields. Flexible SERS substrate have several advantages but there are certain drawbacks including interference of fluorescence. Fluorescence can arise from the sample itself or from impurities in the sample or the SERS substrate. It can interfere with the Raman scattering signals and reduce the sensitivity and accuracy of SERS measurements. Another challenge is the low reproducibility of measurements. The reproducibility of SERS measurements can be affected by factors such as the quality and uniformity of the SERS substrate, the stability of the substrate under different environmental conditions, and the signal-to-noise ratio of the Raman spectrometer.

### 3.4 Reusable SERS substrate

The ability of SERS substrates to be reused is an important factor for their practical application. The development of reusable SERS substrates can not only reduce the cost of the sensors but also enhance their environmental sustainability. One approach to developing reusable SERS substrates is to prevent the analytes from infiltrating into the substrate (Zhang et al., 2019a). By introducing hydrophobic materials to the substrate surface, the aqueous solution of the sample can be prevented from accessing the substrate, making it possible to directly measure liquid samples without waiting for the sample to dry. This approach can improve the detection

speed and efficiency of the SERS sensors. Moreover, materials with photocatalytic activity, such as  $TiO_2$  and  $C_3N_4$  nanosheets, can be introduced to achieve the degradation of the analyte molecules on the SERS substrates, which can enable the substrates to be reused (Hsu and Chen, 2015; Qu et al., 2019a). **(Table 1)** 

3.5 SERS substrate with precision sensing capabilities

In practical SERS applications, accuracy can be compromised by complex sample matrices and impurities (Pang et al., 2014). To address this, selective detection strategies have emerged, utilizing molecularly-imprinted polymers, antibodies, aptamers, and specific chemical reactions to mitigate interference (Chen et al., 2012). For instance, Chen et al. (2012) devised a SERS sensor employing a chemical reaction between Hg<sup>2+</sup> and sodium 2-mercaptoethanesulfonate (mesna) to selectively detect Hg<sup>2+</sup>. The antibody-SERS method combines antibody-antigen specificity with SERS sensitivity to detect complex systems, exemplified by Deng et al. (2019) utilizing Ag@Au bimetallic nanorods modified with Sudan I antibodies. Aptamers (**Table 1**), single-stranded oligonucleotides with specific three-dimensional structures, offer high affinity and specificity for target molecules, demonstrated by Pang et al. (2014) (**Fig 3**) in a SERS sensor for pesticide detection in apple juice. Molecularly-imprinted polymers (MIPs) provide specificity through imprinting processes, as (Feng et al., 2017) showcased in a MIP-SERS sensor for chlorpyrifos detection in apple juice. However, while specific SERS substrates offer advantages, they may limit simultaneous detection of multiple target analytes.

3.6 Assemblage of SERS in microfluidic substates and smartphone devices

Integration of SERS with microfluidic devices (Fig 3) and android systems has broadened its utility across industries. Microfluidic chips, allowing precise fluid manipulation on a micronmeter scale, when combined with SERS, enable detection of pesticides, heavy metals, and antibiotics (Zhou et al., 2015). Zhang et al. (2019b) developed intelligent SERS sensors using microfluidic emulsification, employing charged polyvinyl alcohol (PVA) microgels coated with silver nanoparticles (Ag-NPs) to selectively concentrate molecules via electrostatic interactions. Qi et al. (2014) integrated SERS with a microfluidic platform (Table 1) for rapid quantitative detection of As(III) ions, employing silver nanoparticles functionalized with glutathione and 4-mercaptopyridine. This integration facilitated the sensitive quantification of As(III) ions in water samples, achieving a low detection limit of 0.67  $\mu$ g/kg. Kim et al. (2012) achieved on-site detection of melamine in milk using portable Raman spectrometers and nanocolumn arrays as SERS substrates, demonstrating a detection limit of 120 ng/kg in

aqueous solution. Dou et al. (2015) focused on selective enhancement of SERS signals of  $\beta$ agonists in pig hair extracts using gold nanoparticles loaded on microfluidic paper chips, achieving a low detection limit in the ng/ml range. This convergence of SERS with mobile technology, such as smartphones, enables on-site contaminant assessments with user-friendly operation and data sharing capabilities (Li et al., 2019). Smartphone-based VOC fingerprinting platforms offer cost-effective solutions for non-invasive field detection of plant diseases such as late blight, showcasing the versatility and potential of SERS in various applications.

**3.7** SERS substrate and agriculture tool

Quantitative analysis techniques are pivotal in analytical science, offering precise and efficient methods for collecting complex data, notably from spectroscopic techniques such as Raman and SERS. Through advanced algorithms and statistical models, quantitative analysis determines analyte concentrations or properties within samples, aiding in composition understanding, contaminant identification, quality assessment, and change monitoring across diverse fields such as chemistry, biology, and environmental science. Integration of spectroscopic techniques with robust quantitative methodologies bolsters analytical measurement reliability. Partial least squares regression (PLSR), artificial neural networks (ANN), and support vector regression (SVR) are potent tools for extracting information from intricate datasets (Ai et al., 2018). In Raman and SERS, machine learning algorithms can swiftly and accurately identify and classify analytes based on spectral features. Li et al. (2017) utilized an electronic nose (e-nose) and confocal Raman spectroscopy for quantitative pesticide residue detection in tea, employing ANN models to correlate signals with residue concentrations. Wang et al. (2018) devised a D-SERS and random forest (RF) algorithm combination for fenthion detection on fruit and vegetable peels, ensuring rapid and accurate outcomes. Zhu et al. (2021) introduced a novel method merging SERS with a one-dimensional convolutional neural network (1D CNN) for pesticide residue identification in tea, showcasing the potential of deep learning and artificial intelligence in efficiently analyzing large and complex spectral data, particularly in agricultural samples (Fig 3).

#### 4.0 Application of SERS for agri-food analysis

In agricultural and food safety analysis, chromatographic-based techniques such as gas chromatography (GC) and high-performance liquid chromatography (HPLC) coupled to mass spectrometry (MS) are considered the gold standard methods for analyte detection (Perumal et al., 2021). These techniques offer high sensitivity, selectivity, and accuracy in identifying and quantifying various compounds in complex samples. These methods require dedicated

laboratory space, expensive equipment with high upkeep costs, and trained operators. Additionally, they involve complex analyte extraction and time-consuming sample preparation steps. SERS offers a comparatively simpler approach as an alternative for the detection of analytes in food (Zhang et al., 2020) (Fig 4). In the following sections we will review the application of SERS for the qualitative and quantitative analysis of agricultural related analytes including heavy metals, pesticides, antibiotics, additives, micro- and nanoplastics (Table 2), which address many of the shortcomings of GC, HPLC and MS methods.

4.1 Detection of nutrients and plant stress

### 4.1.1 Detection of nutrients

Consuming food rich in essential micronutrients and macronutrients is vital for maintaining a healthy body and supporting proper functioning of organs. Analysing the nutritional content of food products is essential to ensure their quality and nutritional value. While established techniques exist for nutrient analysis, there are challenges in extracting the analytes and conducting the analysis efficiently. Traditionally, nutrient analysis is performed in a laboratory setting using bulky instruments and time-consuming processes. This makes it difficult to obtain real-time results and ascertain the quality and nutrition level of food on the go. However, the use of optical techniques can offer a potential solution by providing high sensitivity and reliability in a portable format for on-site detection. Portable Raman devices can be used for on-site analysis, offering a quick and reliable method for assessing the nutritional content of food products. Radu et al. (2016) utilized a SERS method for the simultaneous detection of two variants of vitamin B, riboflavin, and cyanocobalamin, in cereal fortified with vitamins (Table 2). The researchers fabricated SERS-active substrates in-house using e-beam lithography on a silicon wafer, followed by the deposition of a gold layer. A label-free SERS technique (Zanuttin et al., 2019) was developed for the characterization of white wine. The study included the analysis of 180 wine samples, specifically focusing on three different white wine varieties: Sauvignon Blanc, Ribolla Gialla, and Friulano. These samples were collected from three distinct Italian wine producers located in the northeastern Italy region. Other nutrient-related components such as flavonoids and antioxidants have also been studied using SERS. Aguilar-Hernández et al. (2017) focused on the utilization of silver colloids as an enhancing medium for surface-enhanced Raman spectroscopy (SERS) detection of phenolic antioxidants. Specifically, the researchers targeted four phenolic acids: caffeic acid (CA), ferulic acid (FA), p-coumaric acid (4CA), and sinapic acid (SA). The combination of SERS

detection using silver colloids and chemometric analysis with PCA offered a comprehensive approach for the identification and classification of phenolic antioxidants.

SERS sensors are commonly used for the analysis of liquid analytes; they can also be adapted for the detection of gaseous substances with the appropriate sensor design. Park et al. (2020) focused on the development of a novel SERS substrate for the detection of volatile organic compounds (VOCs) emitted from living or preserved plant materials. The researchers achieved this by depositing a layer of silver-nanosphere (Ag-NS) on a Tenax-TA polymer film. The film-based SERS substrate demonstrated its ability to adsorb and detect naturally evaporated volatile organic compounds (VOCs) from three validated VOC standards. This allowed for discrimination between the three standards while also detecting differences in VOC emission at different collection times.

SERS, has also been employed for inorganic molecular detection, but the technique is not ideal due to low Raman cross-sections. Brackx et al. (2020) introduced a novel method for  $Zn^{2+}$  ion detection in water, a surrogate for contamination ( $Zn^{2+}$  presence hints at various pollutants). Using SERS, researchers boosted sensitivity for  $Zn^{2+}$  in water. This technique, therefore, shows promise for food characterization, offering superior sensitivity and rapid analysis. Future research may aim for quicker analysis by bypassing lengthy extraction steps and employing stable, pH-resistant nanoparticles. While SERS in food analysis is nascent, further advancements are expected, paving the way for widespread adoption in food safety assessment. *4.1.2 Detection of plant stress related response* 

Plant stress can emanate from a multitude of sources, encompassing biotic factors such as pathogens and pests, as well as abiotic factors including drought, heat, or nutrient deficiencies. These stressors wield deleterious effects on plant growth, development, and reproduction. In response, plants have evolved intricate tolerance mechanisms. Detecting early signs of plant stress and pinpointing their origins are imperative for mitigating potential yield losses and ensuring high-quality produce. Non-destructive or minimally invasive analytical techniques are highly coveted in this pursuit. SERS emerges as a particularly advantageous tool due to its non-destructive nature and minimal or non-existent sample preparation requirements. SERS holds unique promise for plant stress analysis, offering the ability to conduct repeated measurements on the same plant over time, facilitating the monitoring of stress dynamics and the evaluation of stress mitigation strategies. For instance, Zhang et al. (2018a) devised a swift SERS-based method for detecting residual synthetic cytokinins, specifically 6-benzylaminopurine (6-BAP), a common plant growth stimulant and regulator in stress

responses (Table 2). Anthocyanins, pigments produced in response to abiotic stressors, play crucial roles in plant adaptation and protection. Zaffino et al. (2015) developed a SERS sensor specifically for detecting anthocyanidins, the aglycones of anthocyanins, showcasing distinct spectral differences among various derivatives. Moreover, innovative SERS techniques enable real-time monitoring of pesticide penetration within plant tissues, exemplified by Yang et al. (2019a) in their study on thiabendazole (TBZ) in tomato plants. Further advancements include Wang et al. (2017a) development of a SERS technique for detecting aromatic plant hormones and Bai et al.'s (2017) ultrasensitive SERS assay for dipicolinic acid (DPA), a biomarker for bacterial spores. The latter demonstrated a LOD of 0.01 µg/kg using an indirect SERS method, highlighting its remarkable sensitivity. Traditional SERS methods may require sample destruction or invasive preparation, hindering real-time, non-destructive monitoring of plant health. To address this, imaging-based SERS methods have emerged, integrating Raman microscopy or hyperspectral imaging to visualize and analyze plant chemical composition longitudinally and non-destructively. Nonetheless, challenges persist, including reproducibility in complex food matrices and the need for large tissue volumes for validation (Crawford et al., 2019; Wang et al., 2019b). Addressing these challenges necessitates optimizing experimental conditions, standardizing measurement protocols, and exploring representative sampling strategies. Furthermore, combining chemometric methods with spectral data analysis can enhance quantitative measurements, contributing to the continued progress and application of SERS in food safety and plant health assessment.

4.2 Detection of contaminants and chemicals

### 4.2.1 Detection of pesticides

SERS has emerged as a highly promising method for detecting and monitoring pesticide residues in food, offering significant advantages over traditional chromatographic techniques. This technique, particularly when applied to surface sampling techniques like fruit peels, has proven to be effective in routine food screening (Gong et al., 2019; Yang et al., 2016b). SERS presents multiple advantages over chromatography, including label-free direct detection, high sensitivity, and the ability to discriminate between different pesticide classes on plant surfaces with minimal or no sample preparation. The advent of portable Raman spectrometers has further facilitated its application, enabling on-site measurements and rapid screening without the need for extensive sample transportation and processing. Portable SERS sensors have greatly improved the accessibility and usability of this technology for pesticide detection, allowing for in situ detection of various pesticides on fresh produce. Numerous studies have

successfully detected pesticides such as ferbam, thiram, thiabendazole (TBZ), methyl parathion, and many others using direct SERS methods (Guo et al., 2015a; Hou et al., 2015, 2017; Mandrile et al., 2018; Tite et al., 2017; Wang et al., 2015a; Xu et al., 2017; Yuan et al., 2017; Zhou et al., 2016; Zhu et al., 2018). Various SERS techniques employ different sampling methods to simplify the analysis process. These methods include swabbing with flexible SERS substrates, using cotton swabs, or applying SERS-active tape through a "press and peel-off" approach (Hou et al., 2015; Suresh and Yap, 2015; Wang et al., 2017b). For instance, researchers have developed gecko-inspired nanotentacle substrates that mimic the adhesive properties of gecko feet, allowing for easy sampling and direct detection of pesticides (Wang et al., 2017c). Another approach involves using sticky tapes as SERS substrates, providing an alternative method for analyte collection from various sample surfaces. Adhesive tape debcorated with gold colloidal particles has been developed as a SERS tape sensor specifically for detecting pesticides in fresh produce (Chen et al., 2016). Additionally, colloidal bipyramid gold nanoparticles (BP-Au-NPs) have been utilized as an enhancing medium for SERS detection of trace pesticides on agricultural products, resulting in a sensitive detection method (Wu et al., 2019). Incorporating graphene into flexible SERS substrates has also been explored for pesticide detection. Graphene's high adsorption capability for organic aromatic compounds facilitates the enrichment of pesticide analytes on the SERS substrate, leading to enhanced detection sensitivity Sun et al. (2017) (Table 2).

Understanding the penetration profiles of pesticides in fresh produce is crucial for ensuring food safety (Chen et al., 2019; Fateixa et al., 2018; Yang et al., 2016b) (Fig 5). SERS mapping methods with Au-NPs provide valuable insights into pesticide penetration, aiding in the development of effective pesticide application and residue management strategies (Yang et al., 2016b). By visualizing and mapping the distribution and depth of pesticide penetration within produce, these techniques contribute to reducing systemic pesticide residues and maintaining food quality.

### 4.2.2 Detection of contaminant and toxins

Detecting contaminants in food is pivotal for safeguarding human and animal well-being. These contaminants, ranging from metals and plastic fragments to chemicals and toxins, present substantial health risks. In this context, SERS has emerged as a promising analytical method for identifying contaminants and toxins in food due to its ability to offer rapid and sensitive analysis, facilitating early detection and monitoring throughout the food supply chain.

However, despite its potential, further research is imperative to refine techniques, ensure reproducibility, and broaden the scope of detectable contaminants.

Researchers have extensively explored the application of SERS for detecting various contaminants in food, including heavy metals, pesticides, mycotoxins, and microbial toxins (Perumal et al., 2021). Ko et al. (2015) introduced an innovative SERS technique for detecting aflatoxin B1 (AFB1) at trace levels. AFB1, a mycotoxin produced by fungi, poses significant health risks in contaminated food products. The researchers employed magnetic beads for AFB1 separation and silica-encapsulated hollow gold nanoparticles (SEHGNs) as the SERS substrate, demonstrating potential for rapid and reliable AFB1 detection. Janči et al. (2017) focused on developing a rapid and straightforward SERS method for detecting histamine contamination in fresh fish. Histamine, a toxic compound formed during fish spoilage, signals potential foodborne illnesses. Utilizing silver colloids for signal enhancement, the researchers successfully detected histamine, validating their results with high-performance liquid chromatography (HPLC). Pinzaru et al. (2018) delved into SERS for lipophilic toxin detection, employing silver nanoparticles (Ag-NPs) to classify marine biotoxins based on unique spectral features. By analysing SERS spectra, they successfully differentiated structurally similar biotoxins, shedding light on molecular adsorption mechanisms. Lin et al. (2008) showcased SERS's capability to detect melamine in various food products, outperforming HPLC methods with significantly lower detection limits. Fang et al. (2016) addressed illegal drug doping in dietary supplements using a two-step approach combining thin-layer chromatography (TLC) and dynamic surface-enhanced Raman spectroscopy (DSERS) for real-time drug detection. Synthetic colorants in food, subject to stringent regulations, were detected using SERS by (Meng et al., 2016), employing gold nanodumbbells as a substrate for ultra-trace colorant detection in orange juice and cola samples. Additionally, Qu et al. (2019) developed a 3D SERS substrate for tetracycline hydrochloride detection, aiming to enhance sensitivity and selectivity. SERS has also shown promise in detecting polychlorinated biphenyls (PCBs) (Sun et al., 2016), with Zhou et al. (2016) utilizing self-assembled Ag nanocubes on a flexible polyethylene film as a SERS substrate for rapid PCB detection. This template-free fabrication method offers simplicity and flexibility for point-of-care PCB detection, demonstrating high sensitivity and reproducibility (Huang et al., 2018b; Sun et al., 2016). Addressing the spectre of food adulteration and contamination, innovative techniques are vital to ensure the authenticity and safety of the food supply. Traditional methods, often cumbersome and confined to specialized laboratories, are inadequate to meet the evolving regulatory demands and consumer awareness.

Researchers are increasingly turning to SERS, harnessing its exceptional signal enhancement capabilities to detect a wide array of contaminants—from heavy metals and pesticides to toxins and fraudulent substances—entangled within our food products.

### 4.3 Detection of food borne pathogens

Foodborne illnesses pose a significant global public health concern, arising from the ingestion of contaminated food containing pathogens like bacteria, viruses, parasites, or toxins. These contaminants infiltrate food at various stages, spanning production, processing, transportation, storage, and preparation. Factors such as inadequate hygiene, improper storage temperatures, and cross-contamination between raw and cooked foods exacerbate this issue. Under-reporting of cases further complicates efforts to tackle foodborne diseases, skewing assessments of their true prevalence. In addressing this challenge, Cho et al. (2015) introduced a SERS membrane filtration-based sensor, targeting Escherichia coli (E. coli) O157:H7 in ground beef. This method involved bacterial filtration and silver nanoparticle concentration, followed by SERS analysis, enabling selective capture and detection of the bacteria. Prakash et al. (2020) expanded on this approach, employing bimetallic nanoparticles for detecting E. coli, Bacillus subtilis, and Salmonella typhimurium, enhancing sensitivity through bacterial aggregation on the substrate. Hwang et al. (2016) innovated a SERS-based lateral flow immunoassay (LFA) for staphylococcal enterotoxin B (SEB) detection, addressing limitations of conventional LFAs. They utilized Raman reporter-labelled hollow gold nanospheres (HGNs) as SERS probes, improving sensitivity and quantification capabilities. Wang et al. (2017c) presented a label-free detection method utilizing plasmon active nanoparticles assembled onto a 3D bioinorganic super crystal. This approach, employing vancomycin for selectivity, facilitated the identification of gram-positive and gram-negative bacteria through distinct Raman spectra. Advancements in photonics have facilitated the development of sensitive and portable Raman spectrometer systems, enhancing SERS applications in food safety and plant health assessment. These technologies hold promise for mitigating foodborne illness risks, enabling rapid and accurate detection of pathogens throughout the food supply chain.

**4.4** Detection of effector molecules

Stressful conditions, both abiotic (non-living factors) and biotic (living factors), pose significant challenges to the growth, development, reproduction, and yield of plants and animals. While plants and animals share some mechanisms to tolerate and cope with unfavourable stress, plants, in particular, have evolved complex response systems to deal with stressors, as they lack a well-defined immune system. In this response system, plants generate

a multitude of effector molecules that play crucial roles in their stress response. Monitoring and detecting these effector molecules can provide valuable insights into the tolerance mechanisms of plants. The applications of SERS in detecting effector molecules in plants have gained attention and are being explored for various purposes. SERS can detect molecules at very low concentrations, allowing researchers to study subtle changes in effector molecule levels during different stress conditions. By monitoring effector molecules, researchers can gain insights into the signalling pathways and biochemical processes involved in the plant's response to stress. SERS can also provide information about the spatial distribution and localization of effector molecules within plant tissues. This spatial information is crucial for understanding the specific roles of different effector molecules in different plant organs or cell types. It can help identify the sites of effector molecule production, their transportation within the plant, and their accumulation in response to stress. Furthermore, SERS-based detection of effector molecules can be used for early stress diagnosis in plants. By identifying specific effector molecules associated with stress conditions, it may be possible to detect stress responses at an early stage, allowing for timely interventions to mitigate the negative effects on plant growth and yield.

### 4.4.1 Detection of Reactive Oxygen Species (ROS)

Reactive oxygen species (ROS), such as hydrogen peroxide ( $H_2O_2$ ) and superoxide anion radical ( $O_2$ ), are important physiological metabolites in plants and animals that are involved in various cellular processes, including cell signal transduction, growth, development, and responses to biotic or abiotic stress (Moon et al., 2014; Li et al., 2012b). However, when plants are subjected to stress, such as drought, high salinity, or high temperatures, the production of ROS in the plant increases significantly, leading to an imbalance in ROS homeostasis. This imbalance causes oxidative damage to membrane lipids, proteins, and nucleic acids, ultimately resulting in cellular dysfunction and even cell death. In addition to their damaging effects, ROS also play a crucial role as signalling molecules in plants. They are involved in regulating various stress response pathways, including stomatal closure, antioxidant defence, and programmed cell death. Therefore, accurate measurement of ROS is essential for understanding the plant's stress tolerance and regulation.

The study conducted by Chen et al. (2017) presents a dual sensor for hydrogen peroxide ( $H_2O_2$ ) based on SERS and electrochemical detection. The sensor was fabricated using silver nanowires deposited on a coffee filter through a dip-coating method. Additionally, they also

deposited silver nanowires on fluorine-doped tin oxide (FTO) glass, which served as both the SERS substrate and the electrochemical sensor for  $H_2O_2$ .

Dong et al. (2015) proposed a novel approach for the detection of  $H_2O_2$  using a free radicalquenched SERS probe. The probe consisted of gold nanoshells coated with a protective layer of starch, which serves as the enhancement substrate. The signal molecule, methylene blue, is then adsorbed onto the starch-coated gold nanoshells. In this system,  $H_2O_2$  is involved in the generation of free radicals. The free radicals react with methylene blue, leading to the quenching of its SERS signal. This quenching mechanism allows for the detection of  $H_2O_2$ through changes in the SERS signal intensity of methylene blue.

### 4.4.2 Detection of Enzymatic Antioxidants

The excess production of reactive oxygen species (ROS) in plants under stress conditions is counterbalanced by the antioxidative defence system. The antioxidative defence system includes both enzymatic and nonenzymatic antioxidants that work together to scavenge excess ROS and maintain ROS homeostasis in plants (Pang et al., 2011). Enzymatic antioxidants are proteins that are involved in the breakdown and removal of excess ROS. These enzymes include ascorbate peroxidase (APX), catalase (CAT), superoxide dismutase (SOD), peroxidase (POD), and glutathione reductase (GR) (Cao et al., 2017; Chen et al., 2013; Das et al., 2016; Qi et al., 2010). Each of these enzymes plays a specific role in the detoxification of ROS, and their activity can be measured to evaluate the antioxidant status of plants.

SERS has been utilized for the rapid and sensitive detection of antioxidant enzymes. One example is the measurement of horseradish peroxidase (HRP) and its activity using single-molecule SERS. In this approach, SERS is employed in combination with polymer-bridging flocculation to aggregate silver nanoparticles (Ag-NPs). The polymer acts as a bridge, bringing the Ag-NPs together and forming aggregates (Kahraman et al., 2010). By introducing the target enzyme, HRP, into the system, its activity can be measured based on the changes in the SERS signals of the Ag-NPs.

Cottat et al. (2015) presented a novel SERS nanobiosensor for the detection of manganese superoxide dismutase (MnSOD). The sensor utilizes gold nanoantennas and thiolated aptamers to achieve high specificity and sensitivity in MnSOD detection.

### 4.4.3 Detection of Non enzymatic Antioxidants

Nonenzymatic antioxidants, on the other hand, are small molecules that directly scavenge ROS. These antioxidants include glutathione, chlorophylls, ascorbic acid (vitamin C), carotenoids, and tocopherols (vitamin E). They act as scavengers of excess ROS and protect cellular

components from oxidative damage. Detection of these non-enzymatic antioxidants can also confirm the health of a plant (Li et al., 2012b). Lian et al. (2015) demonstrated the application of SERS for the detection of chlorophyll in vegetable oils. One notable aspect of their approach is that it eliminates the need for sample pre-treatment and significantly reduces the testing time. The study identifies spectroscopic markers specific to Cu-Chl and demonstrates a detection limit of 5 mg/kg. The method was applied to analyse a series of commercial vegetable oils, and the results were validated by a government agency as reported by the authors. The findings highlight the potential of SERS-based assessment as a highly effective means of rapidly identifying the presence of trace amounts of Cu-Chl in vegetable oils.

Huang and Chen, (2018) developed a SERS sensor for the analysis of catechin, a natural flavonoid compound known for its various biological effects. In the analysis of catechin using SERS, the relative abundance of catechin in the sample, as well as the presence of citrate-capped Ag-NPs and the aggregation agent NaCl, are crucial factors influencing the quality of detection. By adjusting the component volume ratio to 6:2:1 (catechin:Ag-NPs:NaCl), catechin can be detected at micromolar ( $\mu$ M) levels. Remarkably, when the ratio is further adjusted to 12:2:1, Raman signals become discernible even at molar (10–18 M) concentrations. These conditions promote optimal performance of the SERS mechanisms and the force exerted by laser tweezers. The significant signal enhancement achieved under these conditions allows for an ultrasensitive and reproducible determination of catechin through Raman spectroscopy.

### 4.4.4 Detection of plant hormones

Plant hormones are naturally occurring trace organic compounds synthesized within plants. They serve as chemical messengers and play vital roles in regulating plant physiology during growth, development, and in response to biotic and abiotic stresses. There are nine recognized types of plant hormones that have been extensively studied; they are auxins (such as indole-3-acetic acid, IAA), cytokinins (such as zeatin), gibberellins (such as gibberellic acid, GA), ethylene, abscisic acid (ABA), brassinosteroids (BR), jasmonates (JA), salicylic acid (SA), strigolactones (SL). In addition to these recognized plant hormones, other compounds such as nitric oxide (NO), cytochrome P450s, protein kinases, and polypeptides have similar physiological actions and are considered as plant hormone analogues. The occurrence and content of these hormones depend on factors such as the plant organ, plant age, developmental stage, environmental conditions, and stresses (Song et al., 2016; Wang et al., 2015b; Yuan et al., 2016). Their precise balance and interactions are crucial for the proper growth, development, and response of plants to their environment.

The rapid and sensitive analysis of trace N<sup>6</sup>-Benzyladenine in a complex matrix has been achieved using SERS with a gold nanoparticle colloid substrate (Wu et al., 2014; Zhang et al., 2018b). The study conducted by Chen et al. (2017) presents a novel approach for the trace detection of brassinosteroids using a label-free gold nanoparticles (Au-NPs)-immobilized paper strip with SERS effects. SERS has been extensively used for monitoring nitric oxide (NO) in complex matrices. By integrating Raman reporter molecules with SERS-active nanostructures that interact with NO, changes in SERS spectra can be induced, enabling the detection and analysis of NO. Cui et al. (2016) utilised o-phenylenediamine-modified gold nanoparticles (Au-NPs) as nanoprobes for the detection of NO in living cells. The o-phenylenediamine molecules, acting as Raman reporters, were attached to the surface of Au-NPs.

### 4.4.5 Detection of lipid molecules

Lipid peroxidation, which is the oxidative degradation of membrane lipids, is one of the most common and damaging consequences of ROS accumulation. Malondialdehyde (MDA) and arachidonic acid are two commonly used indicators of lipid peroxidation in plants and are often used as markers for assessing the extent of oxidative damage caused by environmental stresses (Ding et al., 2010; Guo et al., 2012). In the context of fatty acid analysis, researchers have developed a simple SERS substrate known as gold-coated horizontally aligned carbon nanotube (Au-HA-CNT). This substrate offers a large active area, which is advantageous for trace analysis of fatty acids (He et al., 2012). The combination of gold coating and horizontally aligned carbon nanotubes provides enhanced Raman signals and a suitable platform for analysis of fatty acids at low concentrations.

#### 4.4.6 Detection of osmotic regulatory substances

Under stress conditions such as salt, cold, and drought, plants experience osmotic stress, which disrupts the osmotic equilibrium within their cells. To cope with this stress, plants employ two primary strategies for osmotic regulation. The first strategy involves absorbing and accumulating inorganic salt ions, which helps restore the osmotic balance by increasing the solute concentration within the cell. This mechanism allows plants to maintain turgor pressure and cell integrity even under stressful conditions. The second strategy involves the synthesis and accumulation of compatible osmolytes, which are small organic molecules. These osmolytes, such as proline, glycine betaine, and soluble sugars such as glucose and fructose (Kong et al., 2013; Sun et al., 2013) (Fig 5), function by lowering the osmotic potential within the cell (Guo et al., 2015b; Sun et al., 2013). By increasing the concentration of these

compatible osmolytes, plants can counteract the effects of osmotic stress, protect cellular structures, and maintain essential cellular processes. Monitoring the contents of these small molecules using SERS is crucial for gaining a deeper understanding of the mechanisms underlying plant stress responses and tolerance. (Qi et al., 2015) designed a "turn-off" SERS sensor for glucose detection. The sensor exploits the etching effect of silver nanoparticles (Ag-NPs) by hydrogen peroxide ( $H_2O_2$ ) generated from glucose in the presence of glucose oxidase (GOx). In this sensor design, 4-mercaptopyridine was used as Raman tags that were attached to the Ag-NPs. When the glucose molecules are present and reacted with GOx,  $H_2O_2$  is produced as a by-product. The  $H_2O_2$  then initiates the etching of Ag-NPs. As a result, the surface area of the Ag-NPs decreases, leading to a decrease in the SERS signal intensity of the 4-mercaptopyridine Raman tags.

#### 4.4.7 Detection of other effectors

The concentration, type, and activity of trace effector molecules, including glutathione and proteins, are known to play crucial roles in the regulatory mechanisms that allow organisms to adapt to various stresses. Monitoring these effector molecules can provide valuable insights into stress responses and adaptive processes. In the context of stress protein detection, SERS using silver nanoparticles (Ag-NPs) as the substrate has been employed to detect trace stress proteins such as HSP70 (Bhardwaj et al., 2013). This technique provides high sensitivity, enabling the detection of low concentrations of proteins. Furthermore, the simplicity of the SERS-based detection method is highlighted, as it requires only a two-step process for HSP70 detection (Ma and Huang, 2015). This simplicity makes it an attractive alternative to traditional multi-step enzyme-linked immunosorbent assay (ELISA) methods. One of the limitations of SERS is the presence of fluorescent effectors. Fluorescent molecules or impurities in the sample can emit fluorescence that overlaps with the Raman signals, making it challenging to accurately detect and analyse the Raman spectra. This fluorescence can mask or interfere with the weak Raman scattering signals, reducing the sensitivity and selectivity of SERS. The presence of fluorescent effectors can also introduce background noise, making it difficult to distinguish the desired Raman peaks from the fluorescence background. To mitigate this limitation, strategies such as spectral filtering, time-resolved measurements, or using SERS substrates with minimized fluorescence background are employed to improve the signal-tonoise ratio and enhance the detection capability of SERS in the presence of fluorescent effectors.

#### 5.0 Comparison of analytical parameters of traditional detection techniques and SERS

In agricultural food analysis, sensitivity, accuracy, and specificity are critical parameters that directly impact food safety and quality assurance. Traditional detection techniques such as chromatography coupled with mass spectrometry, and electrochemical or fluorescence sensors, have been reliable in providing accurate results. However, they may fall short in terms of sensitivity and specificity when dealing with complex matrices like agricultural samples. SERS addresses these limitations remarkably well. Firstly, SERS offers exceptional sensitivity, enabling the detection of analytes at ultra-low concentrations, even amidst the complexity of agricultural samples. This heightened sensitivity ensures that even trace amounts of contaminants or pesticides can be identified, which is crucial for maintaining food safety standards. Moreover, SERS boasts impressive accuracy. By harnessing the inherent specificity of Raman spectroscopy, SERS can accurately identify and characterize molecules within agricultural samples. This accuracy is essential for distinguishing between different compounds, such as pesticides, nutrients, and contaminants, ensuring that the analysis results are reliable and trustworthy. Furthermore, SERS provides excellent specificity. The signal enhancement provided by plasmonic nanoparticles in SERS enables the precise identification of target analytes, even in the presence of interfering substances. This specificity is crucial for discriminating between similar compounds and minimizing false positives or false negatives in agricultural food analysis. When pitted against traditional techniques (Table 3) for detecting foodborne pathogens, SERS emerges as a frontrunner, boasting a suite of advantages that redefine the landscape of food safety detection methods (Han et al., 2011; Hou et al., 2016; Kanayeva et al., 2012; Mollasalehi and Yazdanparast, 2013; Wang et al., 2017d; Zhu et al., 2021). Unlike conventional assays such as Multiplex PCR (Silva et al., 2011) and Real-time PCR (Ruiz-Rueda et al., 2011), which often entail prolonged assay times spanning several hours, SERS sets itself apart with its remarkable speed, delivering results in mere seconds (Lin et al., 2017). This rapid detection capability is not only pivotal for prompt decision-making in food processing facilities but also minimizes the window of contamination, mitigating risks to public health. Furthermore, SERS exhibits unparalleled sensitivity, surpassing the detection thresholds of methodologies like Lateral Flow Immunoassay and Optical Biosensors. With its ability to detect pathogens at concentrations as low as 10<sup>8</sup> CFU/ml (Lin et al., 2017), SERS ensures that even trace amounts of contaminants are swiftly identified, fortifying food safety standards. Its versatility shines through as well, transcending the limitations of single-pathogen detection methodologies such as Mass-based Biosensors (Shen et al., 2011) and Electrochemical Biosensors (Wang et al., 2013) by offering a comprehensive screening

solution for a wide array of microorganisms, including *Klebsiella pneumoniae* and Salmonella. Moreover, the streamlined sample preparation process of SERS, in contrast to the intricate procedures of DNA Microarray (Bang et al., 2013) and PCR (Shukla et al., 2014), not only reduces assay time but also minimizes the likelihood of errors, making it an ideal candidate for high-throughput screening in food production settings. Its non-destructive nature further solidifies its appeal, preserving sample integrity for subsequent analyses.

### 6.0 Impact of SERS on agricultural economy

SERS has the potential to impact the agricultural economy in various ways. One potential application of SERS in agriculture is for the detection and analysis of pesticides, herbicides, and other harmful chemicals that are used in agricultural practices. SERS-based sensors could provide a rapid and sensitive method for detecting and quantifying these chemicals in crops, soil, and water. This would help to ensure the safety of agricultural products and protect consumers from exposure to harmful substances. SERS can also be used to monitor the concentration of nutrients and trace metals in soil, plants, and animals (Fig 6).

This information can help farmers optimize their crop yields and improve the overall quality of their agricultural products. SERS-based sensors could be used for on-site analysis, allowing farmers to determine the nutrient and metal concentrations quickly and accurately in their crops and soil. Moreover, SERS can be used to study the interactions between plants and beneficial microorganisms, including rhizobia, mycorrhizal fungi, and plant growth-promoting bacteria. By analysing the molecular signals produced by these interactions, researchers can develop strategies to improve crop growth, disease resistance, and overall plant health. In conclusion, SERS has the potential to impact the agricultural economy by providing rapid and sensitive detection methods for harmful chemicals, monitoring the nutrient and metal concentrations in crops and soil, and improving crop growth and health. These applications can lead to higher crop yields, improved product quality, and increased profits for farmers.

### 7.0 Future Perspective and Conclusion

SERS is an analytical technique with extremely high sensitivity and specificity based on knowledge of molecular fingerprints. SERS has been applied extensively in various fields and has shown great promise in the detection of trace stress factors and effector molecules. Increased adoption of the SERS technique could bring great benefit to the agricultural sector but is not without challenges. There is a pressing need for biocompatible, stable, inexpensive, and reliable substrates that utilize new nanomaterials with uniformly high enhancement factors. Improvements in substrate design and fabrication can contribute to more consistent and reliable

SERS measurements. Furthermore, the integration of SERS with other analytical techniques can expand its utility and bring additional advantages (Fig 7).

By combining SERS with complementary techniques, such as result verification methods, improved sample preparation procedures, and automated analysis systems, the overall analytical capabilities can be enhanced. SERS technology can further be improved by quantification of multiple targets simultaneously. This would enable a more comprehensive understanding of the complex interactions and responses within live plants and animals under stress conditions. Additionally, the development of transient, in situ, and dynamic analytical methods for trace target detection can provide real-time insights into tolerance mechanisms. Overall, with further development and effort to overcome the existing challenges, SERS holds great potential to become a robust and reliable analytical technique for in-depth studies on tolerance mechanisms in various fields. Continued advancements in SERS technology and its integration with other approaches can pave the way for new discoveries and applications in the future.

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### Author Contributions

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Shouvik Mahanty and Santanu Majumder. The first draft of the manuscript was written by Shouvik Mahanty and all authors (Richard Paul, Ramin Boroujerdi, Eugenia Valsami-Jones, Christian Laforsch) commented on previous versions of the manuscript. Overall Santanu Majumder had the idea for the article, Shouvik Mahanty mostly performed the literature search and data analysis, and all the other co-authors helped drafting and/or critically revising the work. All authors read and approved the final manuscript.

#### Data availability

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

### Ethics approval

This research work does not involve any human participants and/or animals.

### **Consent for publication**

All authors approved the final manuscript for submission

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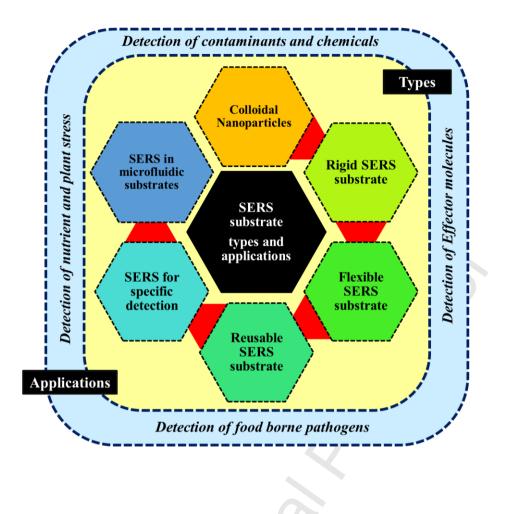
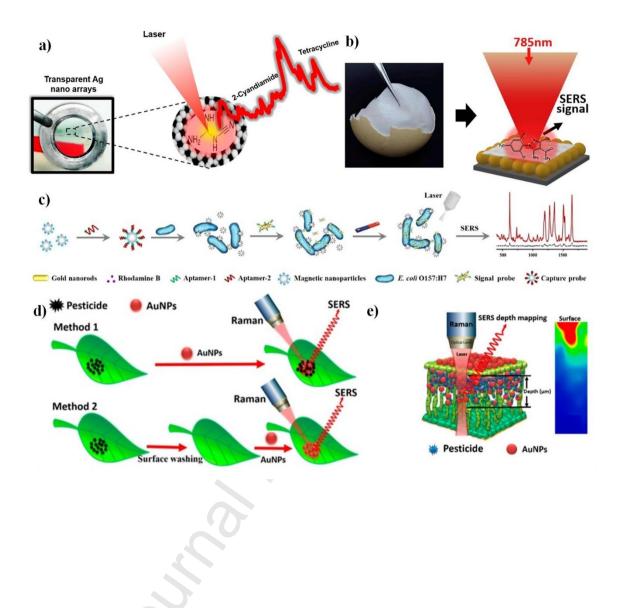
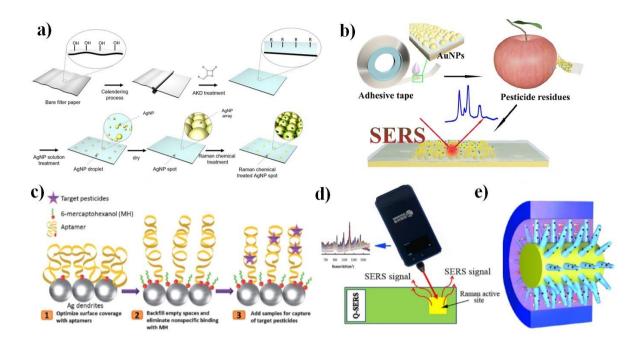


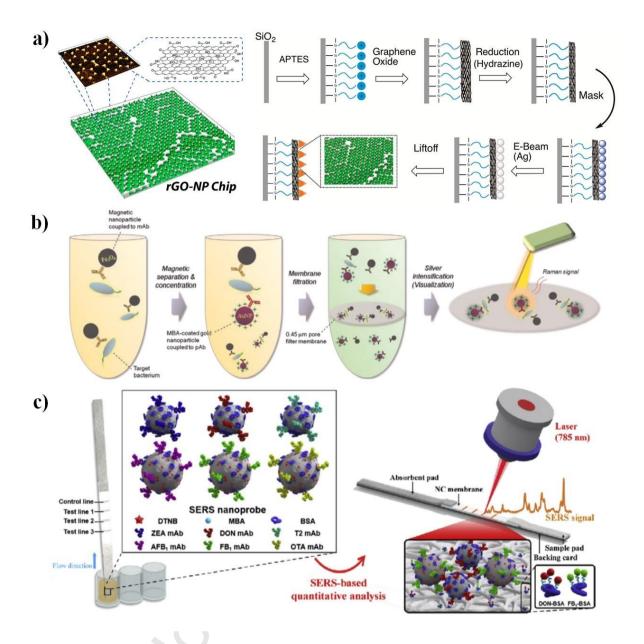
Fig 1. Different types and applications of SERS substrate.



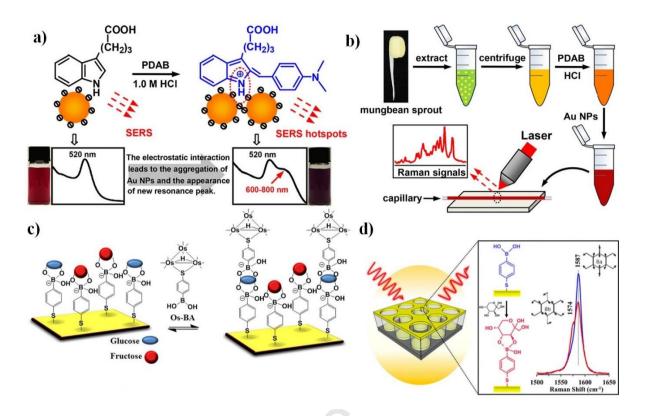
**Fig 2.** Different types of SERS substrate a) detection of Tetracycline and Dicyandiamide in milk using Ag nanoparticle Arrays (Muhammad et al., 2020a) b) detection of fipronil in chicken eggs using SiO<sub>2</sub>@Au core/shell nanoparticles (Muhammad et al., 2020b) c) Au nanobones SERS Aptasensor for detecting Escherichia coli O157:H7 (Zhou et al., 2020) d & e) direct detection of ferbam in spinach leaves without washing surface residues using Au-NPs (Yang et al., 2016a).



**Fig 3.** *a)* Schematic illustration of fabrication process of filter paper-based SERS sensor for the detection of pesticides (Lee et al., 2018) *b*) Schematic illustration of the fabrication of SERS tape and extraction of targets from fruit peel surface (apple) for SERS analysis (Chen et al., 2016) *c*) Schematic illustration of the development of the single aptamer-based SERS method for the detection of four specific pesticides (isocarbophos, omethoate, phorate, and profenofos) (Pang et al., 2014) *d*) Schematic illustration of the collection of SERS spectra using a handheld Raman spectrometer coupled with Q-SERS (Zhu et al., 2020) *e*) A battery-controlled SERS fluidic system (Zhou et al., 2015).



**Fig 4.** *a)* Graphene oxide nanoprisms SERS substrate for the detection of environmentally important aromatic compounds (Shanta and Cheng, 2017) *b)* Schematic for rapid detection of microorganism by SERS substrate made of magnetic nanoparticles coupled with antibody (Cho et al., 2015) *c)* Multiplex SERS-based lateral flow immunosensor for mycotoxins (Zhang et al., 2020).



**Fig 5.** *a* & *b*) Schematic drawing and illustration for the detection of plant hormone in the mungbean sprout by SERS spectroscopy using Au-NPs as Raman amplifier (Wang et al., 2017a) *c*) Transition metal carbonyl probe as a SERS substrate for the detection of Glucose (Kong et al., 2013) *d*) Utilization of 4-mercaptophenylboronic acid (4-MPBA) on the Au quasi three-dimensional plasmonic nanostructure array (Q3D-PNA) for sensitive and fast detection of fructose using SERS (Sun et al., 2014).



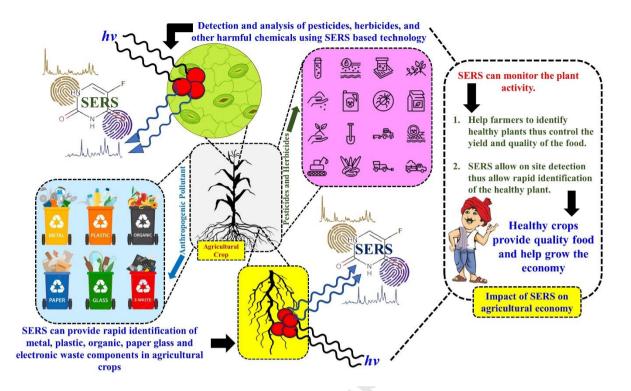


Fig 6. Impact of SERS on agricultural economy.

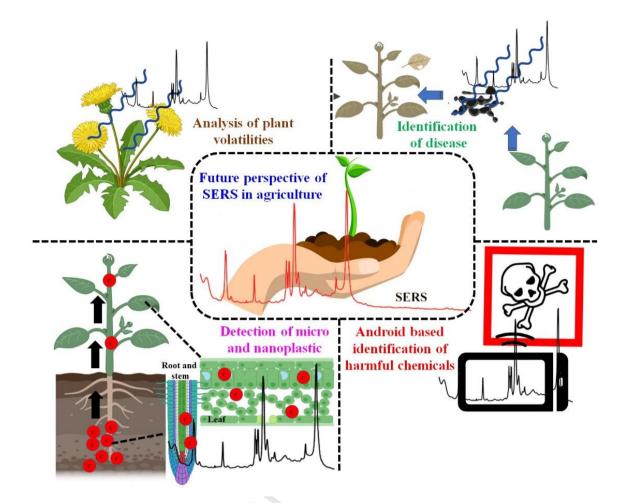


Fig 7. Future perspective of SERS in agriculture.

Sl.No	Types of SERS substrate	Products	Analytes	Reference				
SERS	SERS substrate from colloidal nanoparticles (NPs)							
1.	Silver (Ag)-NPs	Apples	Acetamiprid, Chlorpyrifos and Carbendazim	(Zhai et al., 2017)				
2.	Ag β-cyclodextrin modified NPs	Milk	Norfloxacin	(Qiu et al., 2022)				
3.	SiO <sub>2</sub> @Gold (Au) Core-shell NPs	Eggs	Fipronil	(Muhammad et al., 2020b)				
4.	Au@Ag Bimetallic NPs	Milk	Kanamycin	(Jiang et al., 2019)				
5.	Au nanorods	Romaine lettuce	Escherichia coli O157:H7	(Zhou et al., 2020)				
6.	Au-NPs	Nine-layered pagoda leaf tomato tissue and spinach leaf tissues	Penetration and transfer behavior of pesticides	(Yuan et al., 2017)				
7.	Aptamer-modified SiO2@Au core/shell NPs		Polychlorinated biphenyls (PCB) -77	(Lu et al. 2014)				
Nanos	tructured template-derived rigid SERS substrate							
8.	Aluminum coated Ag nanorod (NRs)	Fruit	Thiabendazole (TBZ) and Tetramethyl Thiuram Disulfide (TMTD)	(Muhammad et al., 2020a; Sun et al., 2016)				
9.	SERS chip	Soil	Organophosphorus pesticides	(Guselnikova et al., 2019)				
Flexib	le SERS substrate							
<i>10</i> .	Ag-NPs in combination with paper	Fruit	Thiram and Ferbam	(Chen et al., 2017a)				
<i>11</i> .	Adhesive tape in combination with Ag-NPs	Fruit and vegetables	Triazophos	(Gong et al., 2019)				
<i>12</i> .	Ag-Nps to the sticky side of the sealing film tape	Cherry Peels	Thiram	Wang et al., (2018)				
<i>13</i> .	Hydrophilic polytetrafluoroethylene ultrafiltration (UF) membrane modified with Au-NPs	Orange peel	Thiabendazole	(Hong et al., 2017)				
14.	Polydimethylsiloxane (PDMS) on silicon wafers and Au nanowires (NWs) on the PDMS surface	Tomato	Methyl Parathion	(Ma et al., 2020)				
15.	Ag-NPs grown in situ on the cotton cloth	Apple peels	Carotene	(Chen et al., 2018)				

**Table 1** Exploring different types of SERS substrate and their applications.

Sl.No	Types of SERS substrate	Products	Analytes	Reference
16.	Chitosan sponge as a flexible substrate and soaked in Ag-NPs		Triazophos	(Wang et al., 2019a)
Reusa	ble SERS substrate	I	1	
<i>17</i> .	Reusable paper-based SERS sensor	Milk	Melamine	(Zhang et al., 2019a)
SERS	substrate with precision sensing capabilities			
18.	2-mercaptoethanesulfonate (MESNA) coated in Ag-NPs	Water	Mercury	(Chen et al., 2012)
19.	Au@Ag core-shell bimetallic NRs modified with the antibody of Sudan I.	Water	Sudan I	(Deng et al., 2019)
20.	Aptamer modified SERS sensor	Apple juice	Profenofos, Phorate, Isocarbophos, Omethoate	(Pang et al., 2014)
<i>21</i> .	Molecularly imprinting polymers (MIPS)-SERS	Apple juice	Chlorpyrifos	(Feng et al., 2017)
Assem	blage of SERS substrate with other microfluidic (	devices and android syste	ems	
22.	Ag-NPs functionalized with glutathione and 4- mercaptopyridin	Water	As(III)	(Qi et al., 2014)
<i>23</i> .	Nanocolumn arrays	Milk	Melamine	(Kim et al., 2012)
24.	Au-NPs loaded on microfluidic paper chips	Pig hair extracts	β-agonists	(Dou et al., 2015)

Sl. No	Pollutants	SERS Probe	Matrices	LOD	Reference			
Nuti	lutrients							
1.	Caffeic acid (CA), Ferulic acid (FA), p- Coumaric acid (4CA) and Sinapic acid (SA)	Silver (Ag) colloids	Water	$2.5 \times 10^{-9} \text{ M}$	(Aguilar-Hernández et al., 2017)			
2.	Volatile organic compounds (VOCs) (E)-2-hexenal, (E)-2- hexenyl acetate, caryophyllene, humulene and isoamyl acetate, whereas α- pinene	Ag-nanosphere (NS) on a Tenax-TA polymer film			(Park et al., 2020)			
Plan	t stress markers							
3.	6-benzylaminopurine (6-BAP)	Gold (Au) colloids	Plant	0.33 µg/ml	(Zhang et al., 2018a)			
4.	Anthocyanins	Ag colloid	Plant		(Zaffino et al., 2015)			
5.	Indole-3-butyric acid (IBA)	Au-NPs	Plant	2.0 nM	(Wang et al., 2017a)			
6.	Dipicolinic acid (DPA)	Au-NPs	Escherichia coli	0.01 µg/l	(Bai et al., 2017)			
7.	Metals							
8.	$\mathrm{Hg}^{2+}$	The stable sandwich structure (MB-TS-hDNA/Au-NPs- sDNA)	Spiked environment water samples	0.08 pM	(Zhang et al., 2018c)			

Table 2 Pollutants in	different substrates	and matrices	detected by SERS.

Sl. No	Pollutants	SERS Probe	Matrices	LOD	Reference
9.	As <sup>3+</sup> and As <sup>5+</sup>	I-leucine as bio-recognition element based on graphene oxide (GO)	Waste water	0.5 mg/kg	(Kumar et al., 2016)
10.	$Cd^{2+}$	Gold nanoparticles modified with trimercaptotriazine	Rice	8 μg/kg	(Zuo et al., 2018)
11.	$Pb^{2+}$	GO based-upconversion nano hybrid materials (NHMs)	Water	1.16 ng/kg	(Annavaram et al., 2019)
12.	Cr <sup>6+</sup>	Silver nanoparticles and lateral flow immunoassays (LFIAs)	Water	0.1 µg/kg	(Liang et al., 2014)
13.	$Zn^{2+}$	The di-2-picolylamine (DPA)- Conjugates triaryl methine (TAM) dye	Water 50 µM		(Lee et al., 2019)
14.	Cu <sup>2+</sup>	Dipicolylamine-based ligand anchored onto plasmonic gold nanoparticles through the sulfur atom of the methylthio group	White wine	7.87 μM	(Dugandžić et al., 2019)
15.	F	Combined diketopyrrolopyrrole with 1- butyl iodide	Water	0.7 nM	(Li et al., 2020)
Pesti	icides				
16.	Thiram, TBZ (Thiabendazole)	Ag-NPs/NC paper-based SERS	Spiked apple and cabbages	Thiram: 0.5ng/cm <sup>2</sup> TBZ: 5 ng/cm <sup>2</sup>	(Chen et al., 2019)
17.	Triazophos	Ag-NPs based SERS	Spiked apples and cherry tomatoes	25 ng/cm <sup>2</sup>	(Gong et al., 2019)
18.	Thiram, melamine	Ag-NPs based microelectrodes	Spiked apple juice, milk and infant formula	Thiram: 115 µg/kg in apple juice and 1.5 mg/kg in milk Melamine: 105 ppb in infant formula	(Dies et al., 2018)

Sl. No	Pollutants	SERS Probe	Matrices	LOD	Reference		
19.	TBZ	Au-NPs on an ultra-filtration membrane	Spiked orange peel	ed orange peel 0.125 μg/g			
Anti	Antibiotics						
20.	Oxytetracycline (OTC)	Ag-NPs	Spiked honey	5 μg/kg	(González et al., 2019)		
<i>21</i> .	Ciprofloxacin (CIP)	Au-Ag heterostructure cubes	Spiked chicken wings	2×10 <sup>-7</sup> M	(Li et al., 2017)		
22.	Polyaromatic hydrocarbons (PAH)	Ag-NRs array	Spiked river water and soil	1 mg/kg in river water and, 10 mg/kg in soil	(Cao et al., 2021)		
23.	Benzo pyrene (BAP), Polychlorinated biphenyl (PCB)	Amphiphilic block copolymer- tethered Au-NPs with polystyrene-b-poly (ethylene oxide vesicles)	Spiked water and soil	10 <sup>-12</sup> g/l for BAP and PCB	(Huang et al., 2018b)		
Add	itive						
24.	6-BAP 6 benzylaminopurine (6-BAP)	Au-NPs	Bean sprouts	0.33 µg/ml	(Zhang et al., 2018a)		
25.	Sodium sulfocyanate, melamine, dicyanide- amide	Ag-NPs deposited chitosan- modified filter paper	Spiked milked powder	Sodium sulfocyanate: 10 mg/l Melamine: 1 mg/l Dicyandiamide: 100 mg/l	(Li et al., 2017)		
26.	Malachite green (MG), Crystal violet (CV)	Au@4-MBA@Ag NRs decorated lab-on-capillary	Spiked shell	0.05 μΜ	(Lin et al., 2020)		
Nan	oparticles and Micropla	istic					
27.	Ag-NPs	Ag-NPs@Ferbam	Spiked environmental water, wheat plants	2 μg/g in wheat plant	(Guo et al., 2016a)		
<i>28</i> .	Ag-NPs	Ag-NPs@4-MBA	Wheat leaf	2 µg/g	(Guo et al., 2016b)		

Sl. No	Pollutants	SERS Probe	Matrices	LOD	Reference
29.	Polystyrene (PS), Polymethyl methacrylate (PMMA)	Au Klarite	Atmospheric aerosol particles extracted from the air in Shanghai		(Xu et al., 2020)
30.	PS, Polyethylene terephthalate (PET), Polyethylene (PE), Polyvinyl chloride (PVC), Polypropylene (PP)	Au-NPs decorated strenebutadiene latex sponge	Snow water, sea water, river water and rain water	0.001 mg/ml	(Yin et al., 2021)
31.	PS	Ag-NPs	Spiked water samples from Kuyun river		(Zhou et al., 2021)
32.	PS	Cellulose hydrogel assisted Au-NRs and Ag-NWs		0.1 mg/ml	(Jeon et al., 2021)
Path	logen				
33.	Escherichia coli	SERS membrane filtration- based sensor	Beef	10 CFU/ml	(Cho et al., 2015)
34.	Escherichia coli, Bacillus subtilis and Salmonella typhimurium	Ag or Au bimetallic nanoparticles (BM-NPs)	Water		(Prakash et al., 2020)
35.	Staphylococcus aureus	Raman reporter-labelled hollow gold nanospheres (HGNs)	Food	0.001 ng/ml	(Hwang et al., 2016)
36.	Escherichia coli and S. xylosus	3D bio-inorganic super crystal	Food	102-103 CFU/ml	(Wang et al., 2017c)
Effe	ctors				
37.	Reactive oxygen species (ROS)	Ag-NWs	Water	1 μM	(Chen et al., 2017b)

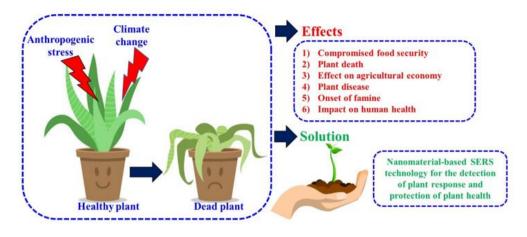
Sl. No	Pollutants	SERS Probe	Matrices	LOD	Reference
38.	ROS	Au nanoshells coated with a protective layer of starch and combination with methylene blue     Water		(Dong et al., 2015)	
Anti	oxidants			X	
<i>39</i> .	Catalase and Pepsin	Colloidal Ag-NPs	Protein films	0.5 μg/ml	(Kahraman et al., 2010)
40.	Manganese superoxide dismutase (MnSOD)	Gold nanoantennas and thiolated aptamers	Body fluids	10 nM to 1µM	(Cottat et al., 2015)
41.	catechin	citrate-capped Ag-NPs	Water	1µM	(Huang and Chen, 2018)
Hor	mones				
42.	Brassinosteroids	Label-free Au-NPs (Au-NPs)- immobilized paper strip	Plant tissue		(Chen et al., 2017a)
<i>43</i> .	Nitric oxides	Au-NPs	Plant tissue	$2.5 \times 10^7$ to $1.0 \times 10^4$ M	(Cui et al., 2016)
Lipi	ds	~'0			
44.	Rhodamine 6G	Gold-coated horizontally aligned carbon nanotube (Au- HA-CNT)	Water	10 nM	(He et al., 2012)

<b>Detection methods</b>	Microorganisms	Assay time	Detection limit	Sample	Reference
Lateral flow immunoassay	Salmonella typhimuium	NA	4.6 ×10 <sup>7</sup> CFU/ml	Tomato	(Shukla et al., 2014)
Multiplex Polymerase chain reaction (PCR)	Salmonella enteritidis	24 h	10 <sup>5</sup> CFU/ml	Chicken	(Silva et al., 2011)
Real-time PCR	Listeria monocytogenes	<30 h	5 CFU/25 g	Meat	(Ruiz-Rueda et al., 2011)
Nucleic-acid sequence-based amplification (NABSA)	S. enteritidis	<90min	10 CFU/ml	NA	(Mollasalehi and Yazdanparast, 2013)
Loop-mediated isothermal amplification (LAMP)	Salmonella, Shigella	<20 h	100 fg DNA/tube	Milk	(Han et al., 2011)
DNA microarray	L. monocytogenes		8 log CFU/mL	Milk	(Bang et al., 2013)
Optical biosensors	Escherichia coli	- ()	$3 \times 10^3$ CFU/ml	Cucumber, Ground beef	(Kanayeva et al., 2012)
Electrochemical biosensors	L. monocytogenes	3h	10 <sup>4</sup> -10 <sup>5</sup> CFU/ml	Lettuce, Milk, Ground beef	(Wang et al., 2013)
Mass-based biosensors	Escherichia coli	4 h	53 CFU/mL	Milk	(Shen et al., 2011)
SERS	Klebsiella pneumoniae, Salmonella	Few seconds	10 <sup>8</sup> CFU/ml	Food	(Lin et al., 2017)

**Table 3** Comparative analysis of the traditional techniques and SERS for the detection of food borne pathogens.

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#### Graphical abstract:



#### Highlights

- \* Review explores nanomaterial-based SERS for crop stress monitoring.
- SERS detects nutrients, pathogens, contaminants, ensuring food safety.
- SERS optimizes crop yields by monitoring soil nutrients and trace metals.
- ◆ Integration of SERS enhances precision, monitors health, defends against threats.
- Economic Impact: SERS boosts yields, quality, and profits.