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Microneedles (MNs)-based Sensing Technology: An Innovative Solution for Agriculture

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Abstract

Agricultural health is one of the most important aspects of improving crop productivity that significantly decreases the demand for food. Plant diseases and nutritional value are among the crucial factors affecting food safety and quality, subsequently reducing the yield of the crops and increasing plant mortality. Therefore, continuous monitoring of plant health is of utmost importance to enhance the yield of the crops. In this aspect, microneedle-based (MNs)-based sensing technology can potentially able to monitor agricultural health. Borrowing a page from medicine, minimally invasive MNs have been effectively used to deliver drugs and biomolecules within the human body without any pain or tissue damage. Usually, MNs have been divided by researchers into four groups: solid microneedles (S-MNs), hollow microneedles (H-MNs), dissolving microneedles (D-MNs), and coated microneedles (C-MNs), which are effectively used according to requirements of delivery of biomolecules and sensing applications. The MNs-based probe is directly attached to the relevant part of the plant tissue, thereby bypassing the cuticles. Interestingly, MNs-based sensing technology offers newer insight into agriculture health by continuously monitoring plant health, including nutritional values and pathogens. This article opens newer avenues and provides knowledge about the fabrication of MNs-based sensing technology for plant health that might benefit the food and agriculture industry.

Key Words: Microneedle, agriculture, sensor, plant disease, continuous monitoring.

1. Introduction

Food requirements relentlessly increase with the growing population and industrialization globally. Moreover, the productivity of the crops decreases with the increasing stress of other things like salinity and pathogens, which exert more pressure on the agricultural and food industries [1-5]. The loss of crops is ~220 billion dollars, whereas approximately 30-35% of the loss of crops globally is due to pathogens. Plant diseases and crop disasters adversely affect the yield of crops, which are some of the most common issues in the agricultural sectors [6-8]. Therefore, it is necessary to develop newer, innovative technologies that improve the yield of crops and protect them from pathogens.

Considerable research and development have been done so far to innovate next-generation technologies and their application in agriculture for real-time monitoring. Such innovative technologies might be beneficial to retain sustainability, food security, and controlling pathogenic

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infection by monitoring plants [9, 10]. Numerous diagnostic technologies such as polymerase chain reaction (PCR), quantitative PCR (qPCR), digital PCR (dPCR), multiplex PCR, enzyme-linked immunosorbent assay (ELISA), fluorescent in-situ hybridization (FISH), immunofluorescence, and flow cytometry has been used for the detection of plants pathogen. However, these laboratory-based detection technologies require skilled workers to analyze, are costly, cannot be monitored continuously, and are inaccessible in remote locations [11-15]. In this aspect, developing inexpensive, rapid, accurate, and early diagnostic sensing devices is necessary.

Early diagnostic sensing devices offer new avenues for monitoring and controlling plant pathogens by providing preliminary information on crop health in a non-destructive manner. The crop's health is important for crop productivity and protection against pathogens. Moreover, sensitivity, robustness, and accuracy are required to retain the sustainability and security of food [13, 14, 16-19]. In this aspect, nanomaterials (NMs) might resolve issues associated with existing technologies.

NMs including metals and their oxide (Cu, Ag, Fe, and Zn, etc.), and carbon-based nanomaterials (CB-NMs) such as carbon nanotubes (CNTs), carbon nanofibers (CNFs), graphene, and graphene oxide (GO), have been efficiently used as the electrode materials for the detection of various analytes of plants including phytohormones, and plant pathogens due to their exceptional properties like high surface area, conductivity, mechanical, and electrical. Moreover, CB-NMs show remarkable triumphs in delivering micronutrients/biomolecules and detecting plant pathogens. However, real-time monitoring of the plants remains a concern [20-29]. Therefore, we need to design electrode materials with specific shapes that can attach to the plants without any adverse effects or damaging plant tissues with the target analytes. In this aspect, microneedle (MNs)-based technology enables innovative platforms to protect agricultural crops and monitor their productivity by reducing agricultural waste and improving nutritional values.

MNs are one of the growing technologies in medicine due to their painless and minimally invasive drug delivery systems. MNs are efficiently used to transdermally deliver numerous macromolecules, and biomolecules such as pharmaceutical compounds, DNA, proteins, and vaccines due to their cost-effectiveness, self-administration, and ease of handling [30-35]. MNs-based sensors easily analyze and monitor the release of drugs, biomarkers, metabolites, and other biological parameters. Undeniably, we have significant evidence suggesting that MNs are efficiently used for diagnostic and therapeutic purposes [36-38]. With the immense success of MNs in biomedical application applications, researchers are attracted to MNs for agricultural applications [39-41]. A few articles based on MNs for agricultural applications, which focused on food, plant treatment, and sensing applications, have already been published. Moreover, specific attention should be required to understand the role of MNs-based sensing technology in the improvement of agriculture systems [39, 40, 42]. MNs-based technologies can bring innovation to farmers and assist them in managing the cause of crop failure, thereby enhancing the productivity of crops. MNs-based technologies also deliver micronutrients, and biomolecules to the plants, controlling

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plant pathogens, sensing pathogens, and monitoring soil and plant health quality. **Fig.1.** shows the graphical representation of the MNs and their application in agriculture especially monitoring plant health.

This perspective focused on the different types of MNs and their fabrication process. MNs-based sensing technology emerged as next-generation tools for minimally invasive monitoring of plant health in real-time. We discussed the MNs-based sensor for monitoring the crops and detecting plant pathogens in real-time. Moreover, we also discussed the role of MNs-based sensors in foods, such as determining quality and detecting pesticides/agrochemicals. Finally, we discuss how we can improve the sensitivity and accuracy of the MNs-based sensor and prospects. Moreover, MNs-based sensing technology enables newer avenues for the detection of analytes even at lower concentrations. This perspective offers new insight for agricultural scientists to understand the newer MNs-based technologies and their application in agriculture.

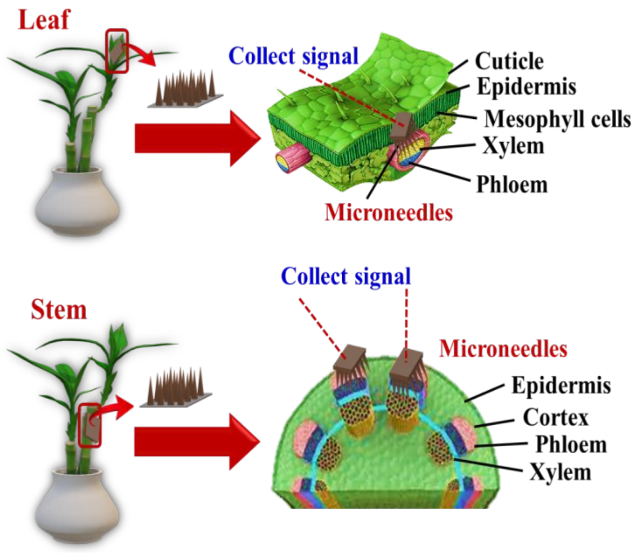

Fig. 1. A schematic illustration of the MNs and their application in agriculture especially monitoring plant health by insertion of MNs onto the surface of leaf and stem.

2. MNs based technology for agriculture

The MNs-based technology was proposed in 1976 and introduced as a transdermal delivery system in 1990, mainly due to the lack of fabrication technology. MNs are micron-size needles (25-2000 mm height) made of various materials, fabrication processes, and shapes. The MNs-based technology is mainly applied in drug delivery systems [43-45]. The tremendous success of MNs-based technologies attracts us towards other research areas, including sensors and agriculture. The minimally invasive technology of MNs provides new insight into the delivery of drugs/biomolecules within the human body without damaging tissues, significantly attracting agriculture researchers [39, 46, 47]. With the help of MNs, we can easily monitor plant health without damaging the plant tissue. Recently, MNs have been used in the agriculture industry to treat diseases, monitor health, and detect agrochemicals/pathogens within the plant, as traditional tools are invasive, relatively less effective, and unable to monitor plant health continuously. Moreover, researchers focused on the efficient, accurate, and fast response of MNs in agricultural systems by modifying materials, shape, size, and space between two MNs and their types [47, 48]. Interestingly, we can also develop an MNs-based micronutrient delivery system and release behavior easily controlled by changing the polymeric matrix. In general, we can say that the fabrication process, selection of materials, and their architecture significantly affect the treatment and detection of plant diseases and their continuous health monitoring. We will further discuss types of MNs and their importance in agriculture.

2.1. Types of MNs

Fabrication of the MNs varies according to the types of MNs and their preferred applications. With the help of different fabrication processes, we can easily develop hollow MNs, honeycomb-like

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structures, angled MNs, and rapidly separating MNs. It is important to mention that the height of the MNs, aspect ratio, substrate diameter, and tensile strength should be considered while designing and manufacturing the MNs. Moreover, high-throughput manufacturing using various resources such as silicon, stainless steel, sugar, and polymers requires a high degree of uniformity, thereby effectively delivering drugs and biomolecules [49-51]. Based on their structure and technique, MNs are divided into four groups: (i) solid MNs (S-MNs), which are made of silicone, glass, stainless steel, and aluminum are often utilized for transdermal testing. Usually, S-MNs create small pores in the epidermis and dermis to effectively deliver drugs, and biomolecules without damaging plant tissues [52, 53]. (ii) coated MNs (C-MNs), the exterior of the C-MNs is layered with a water-soluble medium so that the drugs/biomolecules mix quickly in the membrane after MNs insertion. The covering process should make a thin covering on the exterior of the MNs and sustain adhesion when stored and placed on the membrane. To accomplish it, the covering must have appropriate viscosity. The quantity of drugs or biomolecules that can be loaded based on the film's width and the spike's extent is generally very small [54, 55]. (iii) dissolvable MNs (D-MNs) are made from biodegradable polymers (such as carbohydrates, polyvinyl alcohol (PVA), gelatin, chitosan, and hyaluronic acid (HA)) to encapsulate the drugs or biomolecules to effectively release the drugs/biomolecules [56, 57], and (iv) hollow MNs (H-MNs), have a hollow/hollow core/chamber design where liquid drug is injected/stored to delivered. Interestingly, H-MNs can potentially deliver large amounts of drugs/biomolecules [39, 40, 58]. **Fig. 2.** shows the schematic illustration of the different types of MNs and their application in agriculture.

Unquestionably, there are enough reasons to choose MNs-based technology in agricultural sciences. With the help of technological advancements in fabrication technology, material chemistry, and polymeric sciences it is possible to develop biocompatible, mechanically stable, and biodegradable MNs with numerous designs, which can monitor plant health and pathogens/agrochemicals.

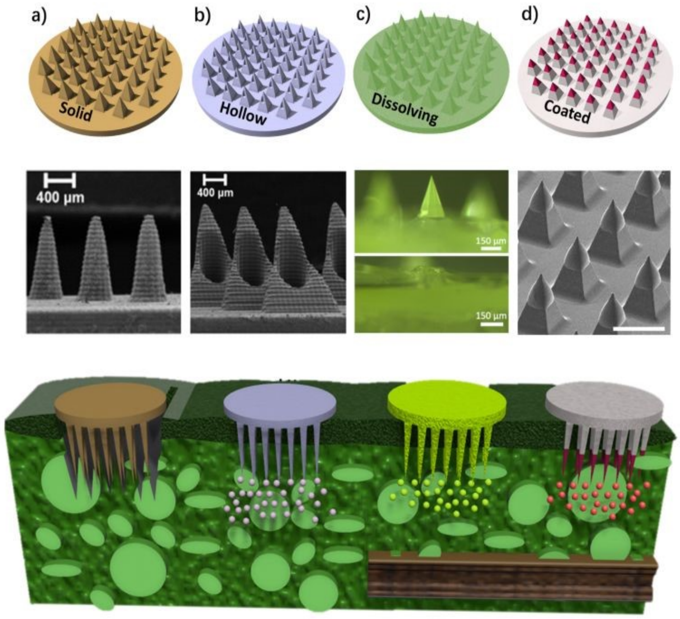

Fig. 2. Types of MNs and their application in agriculture: (a) solid, (b) hollow, (c) dissolving, and (d) coated-MNs. The image was reproduce with permission [40] from Elsevier, copyright @ 2023.

3. It's plenty of possibility for MNs in agriculture

Incontrovertibly, the demands for food endlessly increased due to the growing population and loss of crops globally. The situation becomes more complicated by using grains to produce energy/biofuels in developing countries that employ extra-burden to produce crops [4, 5, 27]. Although, the researchers have made substantial efforts for the production of crops and protection against pathogens. The effective delivery system of agrochemicals, micronutrients, biomolecules, and continuous monitoring of the health of crops are the decisive factors for augmenting plant growth and crop protection. With the advancement of such

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innovative technologies, we can easily achieve high productivity of the crops and high nutritional values with insignificant wastage. Usually, two types of delivery systems are in practice: (1) foliar spray and (2) soil applications. Delivery through soil is most commonly used in agricultural practice, as foliar spray has significantly increased water and soil contamination. Despite the tremendous application of CB-NMs, especially CNTs, CNFs, and GO, for delivering micronutrients, biomolecules, and protection against pathogenic infection in agricultural crops due to their ability to translocate within the plants. However, continuous monitoring of the crop's health remains a concern [27, 59-61]. Therefore, there is a need for such devices that can connect with the plant without damaging their tissues. In this aspect, MNs can potentially transform the agriculture and food sectors.

MNs are extensively used in medicine for the delivery of drug molecules. Unquestionably, we have enough evidence that suggests that the MNs patches effectively delivered the drugs, vaccine, DNA, and proteins to humans and animals without any adverse effects. Numerous studies suggested that inserting and removing MNs patches does not affect/damage plant tissue because of their shape and size. Indeed, we can say that the remarkable discovery of MNs is for the painless delivery of chemical/biological molecules to humans. Researchers are attracted to the MNs for agricultural applications due to their enormous success in medicine. MNs offer plenty of possibilities for agriculture sectors, like micronutrient, agrochemical, and biomolecule delivery, including genes within the plants. Moreover, MNs-based sensing technology easily detects and discriminates the analytes based on the sensing mechanism. Usually, the detection process involves the generation/changes in the signal upon binding with analytes, subsequent increase/decrease in signal intensity with the incorporation of analytes indicates the accuracy of the detection. Likewise, discrimination between various analytes is achieved through the specificity of the targeted analytes. It is important to mention here, that MNs-based sensing technology has the potential ability to accurately detect and discriminate analytes, thereby effectively used in real-time monitoring in agriculture [39, 40, 62, 63]. Additionally, we can make tiny patches of the MNs and attach them to the plants for continuous monitoring of crops. Although, we need to optimize the size and shape of the MNs according to the plants. Indeed, plant-specific MNs-based devices create new wings for agriculture to improve plant health and make next-generation tools for diagnosing plant disease and their developments. MNs-based technology significantly transforms agriculture and food sectors by managing crop health and delivering micronutrients/biomolecules to the plant. Therefore, we can say that plenty of rooms are available for MNs in the agriculture sector.

4. MNs-based sensors in crops

MNs are effectively used in food and agriculture areas due to the variety of materials used in the fabrication. Approximately 600 million people are affected by micro-organisms and foodborne diseases every year. In this aspect, there is a need to develop newer tools/techniques that effectively monitor plant diseases, agrifood issues, and plant growth. MNs can penetrate plants, foods, and soil, thereby easily reaching food matrix and plant tissues. MNs can penetrate plants, soil, and food and reach the food matrix,

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packaging, or plant parts [64, 65]. This provides more accurate and precise information about these elements, enhancing quality control and process management.

4.1. Crop Monitoring

Monitoring the crops is one of the important factors that help improve crop production and protect against pathogens, thereby significantly increasing the research on sensing technologies, especially non-destructive sensors [17, 66, 67]. Usually, the effective management of plant health depends on newer diagnostic assays that should be rapid, sensitive, accurate, and continuously monitored without damaging the plant tissue. However, traditional methods are used to observe plant health that destroys the plant tissues [4, 5, 16, 27]. Researchers developed a thermal probe to measure the movement of xylem juice in tomatoes. Daskalakis et al. developed a thermal sensing device using corn as a model. The MNs-based sensing device measures the differential temperature between leaf and air related to the plant-water stress. Moreover, it can be measured for any plant, soil type, and relative humidity. This device is solar-powered and transmits data wirelessly via an antenna. The prepared backscatter wireless sensor network is a low-cost sensor to monitor agricultural environmental parameters [68]. For more sensor accuracy, researchers think that if the probe is instead within the plants without damaging the tissue, that might revolutionize the sensing technologies in agriculture applications. In this aspect, advancement in sensing technologies is necessary despite the traditional methods used. MNs are a remarkable discovery that is continuously growing attention in drug delivery systems and biomedical devices due to pain-less delivery systems without damaging the tissue. Moreover, MNs open new windows for diagnosing diseases in humans and plants. The advancement in sensing technologies based on MNs effectively analyzes and monitors plant health without damaging plant tissue. For instance, Jeon et al. fabricated an MNs-based device with an impedance system to measure electrical conductivity within the stem of tomato plants. The data indicated that the MNs-based real-time monitoring system measures the tomato plant's salinity. Moreover, understanding the response of nutrients is difficult until the growth of fruits. MNs-based devices have been tested in both greenhouses and fields. The signal noise and electrical conductivity decrease in sensor measurements. Authors believe that the reduction problem can be solved by redesigning the electrical equipment electricity to be suitable for field use [69]. Bukhamsin et al. fabricated MNs using a polydimethylsiloxane (PDMS) mold and developed an MNs-based sensor to measure epidermis barley leaf bioimpedance. MNs were fabricated using PDMS as a substrate material and coated with metal (~500 µm) to enhance mechanical strength. The prepared metal-coated MNs effectively measure bioimpedance in a controlled environment [70]. Wang et al. fabricated an Au-SnO_2-VG-MNs-based sensor for the detection of abscisic acid (ABA) in plants. The data indicate that the ABA is detected by electrocatalytic oxidation due to the synergetic effects of Au-SnO_2 and the exceptional conductivity of vertical graphene. Moreover, the prepared Au-SnO_2-VG-MNs-based sensor has high sensitivity, lower detection limit, and longer-term stability. Additionally, it is important to mention that the MNs less than 700 µm are appropriate for insertion within the plant tissue [62]. **Fig. 3** shows the graphical representation of the fabrication of an Au-SnO_2-VG-MNs-based sensor to detect ABA. Another research group fabricated a three-dimensional (3D) printed-MNs (3D-P-MNs) based electrochemical sensor for real-time monitoring of phytohormone (salicylic acid (SA)) and pH of the cabbage plant. The data indicate that the prepared 3D-P-MNs efficiently measure the SA and pH to

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understand water stress within the plant in real time. Interestingly, 3D-P-MNs-based electrochemical sensors have a low detection limit of ~37 µM. Additionally, the 3D-P-MNs-based sensor precisely measures the live variation of SA through the stem of the plants, thereby easily understanding the unstressed and water-stressed plants [71]. Baek et al. fabricated an MNs-based Sap flow sensor to understand plant physiology via plant leaves. The data indicates that the MNs-based Sap flow sensor effectively observed plant reactions under different environmental conditions, mainly humidity, sunlight, and soil-water content in tomato and bell pepper plants. With the help of this sensor, authors believe that we can easily improve the productivity of the crops [72]. Acanda et al. use Ti-MNs for the GFP expression in citrus plants using agrobacterium infiltration methods. The data indicate that the MNs-roller offers a simple and effective agroinfiltration process for gene expression in citrus plants [73].

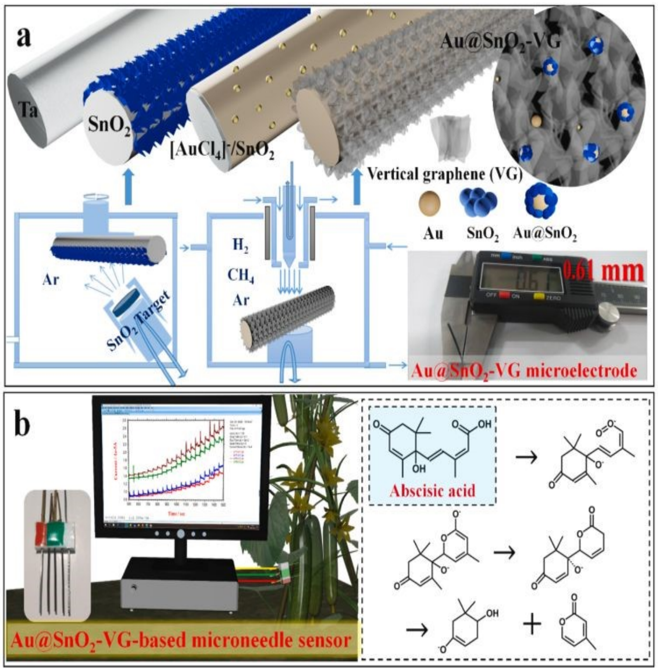

Fig. 3. A schematic illustration of the fabrication of an Au-SnO$_2$-VG-MNs-based sensor to detect ABA. The image was reproduced with permission [62] from Elsevier, copyright @2021.

O'Flynn et al. fabricated Au-Cu-coated-MNs for the analysis of nitrate in soil. The data indicate that the Au-Cu-coated-MNs effectively evaluated nitrate concentration in soil that can analyze real-time growing conditions in agriculture [74]. Cai et al. use SS-MNs to determine the vindoline and catharanthine in the Catharanthus roseus plant [75]. Hegarthy et al. fabricated carbon-loaded polystyrene MNs (C-P-MNs) to monitor tomato leaves' pH continuously. The data indicate that the prepared C-P-MNs effectively detect pH from tomato skin [76]. The aforementioned data and Table 1 suggest that the MNs-based sensing device effectively monitors crop health. It is important to mention here that the diameter of MNs array should be less than 700 µm, easily inserted within the plant tissue without any damage. Furthermore, bioimpedance, pH, stress condition, soil quality, and biomolecules are easily detected using MNs-based sensing devices. With the help of MNs-based sensing technologies, we can easily investigate continuous soil and plant monitoring that might improve their productivity.

4.2. Plant Pathogen Diagnostics

Food security is one global concern affecting the agricultural economy and sustainable goals. Food demand significantly increased with the growing population and simultaneously decreasing agricultural land. Additionally, plant diseases significantly affect the productivity of crops and are one of the common reasons for the failure of crops, leading to extra pressure to improve agricultural crops. Numerous diagnostic technologies such as PCR, ELISA, FISH, IF, and FCM have been used to detect plant diseases. However, these assays require sophisticated instruments, skilled persons, and destructive processes [77]. In this aspect, MNs-based diagnostic devices have the potential abilities to develop non-destructive sensors that can effectively be used to

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monitor plant pathogens continuously. Few studies have been done so far that indicate the effective use of MNs-based sensors for detecting plant pathogens. For instance, Paul et al. fabricated PVA-based MNs using a vacuum-based molding process for the extraction of pathogenic DNA by applying tomato leaves. The data indicate that the PVA-MNs effectively extract the DNA within a min at different plant species. The DNA extraction ability of PVA-MNs helps to detect plant pathogens of late blight disease with a 100% detection rate. Therefore, the prepared PVA-MNs is simple free from cellular lysis, and DNA purification might be revolutionized for molecular diagnosis in plant [78]. **Fig. 4** shows the schematic illustration of the PVA-MNs for extracting pathogenic DNA. Paul et al. fabricated polymeric MNs integrated with a 3D imaging device for loop-mediated isothermal amplification (LAMP) reaction and plant disease diagnosis. The data indicate that the MNs patch can effectively extract nucleic acid from plant leaves using compression and extraction methods within 1 min. The isolated nucleic acid was simultaneously amplified by LAMP using pre-loaded reagents. Next, the smartphone device reader can easily capture fluorescent images of LAMP cassette, thereby easily detect DNA/RNA with 1 pg sensitivity. Therefore, the prepared MNs-based smart phone device has wider applicability in addition to plant health [63]. Another study of a similar group focused on the fabrication of polymeric-MNs patches for the extraction of nucleic acids from various tissues of plants. The data indicate that the MNs easily extract both DNA and RNA from plant leaves [79]. The aforementioned study and Table 1 suggested that the MNs-based sensor effectively detects plant pathogens. The MNs-based *in-vivo* agricultural biosensor might offer on-site, non-destructive information on plant health to improve agricultural cultivation and prevent disease. MNs integrated technology will support the rapid development of precision agriculture, improve food quality, and reduce crop losses. Integration of MNs patches with molecular detection systems using amplification probes (biosensors), fast, cost-effective, simple, and delivery samples can be exposed, exposed, and controlled for plant diseases. The real-time detection of plant pathogens might advantageous that easily treating plants at the initial stage of infection, thereby productivity of crops.

In general, we can say that MNs-based sensing technologies provide newer alternatives to non-destructive extraction of DNA/RNA, which are newer hallmarks of diagnosing diseases using MNs.

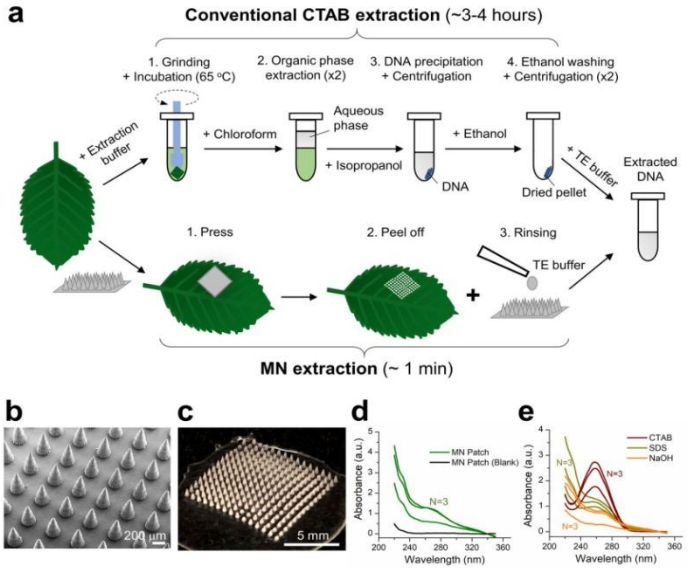

Fig. 4. A schematic representation of the PVA-MNs for extracting pathogenic DNA. (a) schematic of conventional and PVA-MNs based DNA extraction, (b) SEM images of PVA-MNs, (c) photographic image of PVA-MNs patch, (d and e) UV-viz spectra of DNA. The image was reproduced with permission [78] from ACS, copyright @2019.

Table. 1. Different MNs-based sensors for the crop monitoring.

S. No.	MNs	Plants	Analytes	Remarks	Ref
1.	Au-SnO_2-VG-MNs-based sensor	Cucumber	ABA	Effectively detect ABA within the plant, but little damage was observed during plug and	62

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				unplug of the sensor.	
2.	MNs integrated with impedance system	Tomato stem	Salinity of the nutrients	Understanding the nutrients in plants is difficult until the growth of fruits.	69
3.	Metal-coated-PDMS based MNs	Barley leaf	Bioimpedance	Effectively measure bioimpedance of barley leaves at controlled conditions.	70
4.	3D-P-MNs	Cucumber Stem	SA and pH	Effectively measure the live variation of SA.	71
5.	MNs-Sap flow sensor	Tomato and Bell Peppers leave	Sap flow through xylem	Effectively measure sap flow through to under-plant physiology	72
6.	Ti-MNs	Citrus leave	GFP expression	Effectively express the gene in citrus plants.	73
7.	Au-Cu-coated-MNs	Soil	Nitrate concentration	Effectively analyze the nitrate concentration in soil	74
8.	SS-MNs	Catharanthus roseous (leaf, stem, and root)	Catharanthine and Vindoline	Effectively detect anhydrovinblastine within the plant.	75
9.	C-P-MNs	Tomato leaf	pH	Quinone group and carbon change the pH	76
10.	PVA-MNs	Tomato leave	Pathogenic DNA extraction	100% detection of late blight disease	78
11.	MNs integrated device	Tomato leave	Nucleic acid	Virus and fungus infection	63

5. Application of MNs-based biosensors in food

Food supply relentlessly faces the risk of emerging plant diseases caused by micro-organisms like fungi, viruses, and bacteria. Farmers continuously use agrochemicals and pesticides to protect their crops and improve the food's productivity, thereby significantly increasing the crops' average yield and reducing production costs [4, 5, 27]. These agrichemicals and pesticides are commonly found in foods that can cause various diseases like cancer, hormonal imbalance, allergy, asthma, etc. Monitoring the food during supply is essential to confirming food safety and controlling crop loss. Considering this, MNs-based sensing devices have gained significantly increasing interest in monitoring plant and fruit health, which can allow continuous on-site monitoring of fruits and vegetables.

5.1. Pesticide detection

Pesticides are commonly found in fruits and vegetables and are becoming a serious concern globally, as some pesticide residue is complicated to remove and can cause various diseases, including cancer. Therefore, there is a requirement to develop newer sensing technologies to monitor pesticides in foods. Although traditional processes such as gas chromatography (GC) and high-performance liquid chromatography (HPLC) have been used to detect pesticides, which require sophisticated instruments, a skilled person, a time-consuming process, and are difficult to detect on-site [80-82]. In this aspect, MNs-based sensing technologies have the potential ability to monitor pesticides from fruits and vegetables in real-time. Few studies have been done so far that suggest the MNs-based innovative technology to detect pesticides from foods. For instance, Mugo et al. fabricated a molecularly imprinted polymeric (MIP) MIP-MNs-based sensor to detect imidacloprid pesticides from food samples. The MNs-sensor was fabricated using layer-by-layer assembly of CNTs, cellulose nanocrystal (CNC), and imprinted polyaniline layer with co-polymerized imidazole-CNC based film. The data indicate that the IMP-MNs-based sensor has excellent detection ability with a limit of detection of 0.06 µM and reusable ability [83]. Chen et al. coated Au-nanoparticles onto the surface of adhesive tape similar to types of MNs structures for detecting parathion-methyl, thiram, and chlorpyrifos pesticides from apple, orange, and cucumber. The data indicated that the surface-enhanced Raman spectroscopy (SERS) based sensor easily observed the SERS signal to detect pesticides from fruits and vegetables [84]. Mishra et al. fabricated an MNs-based electrochemical sensor to detect organophosphate pesticides. The data suggested that the fabricated MNs-based sensor efficiently detects pesticides that might be used as a wearable sensor for continuous monitoring of toxicity [85]. Yi et al. fabricated novel Ag-PVA-HA-based MNs (PVA-HA-MNs) using PDMS mold to detect thiram and thiabendazole pesticides. **Fig. 5** shows the graphical illustration of the pesticide residue in agricultural products using MNs. The data indicates that the prepared PVA-HA-MNs effectively detect thiram and thiabendazole inside and outer surfaces of the agriculture product with the detection limit of 10^{-7} and 10^{-8}, respectively. The unique stepped structure of the MNs significantly increased the superficial area of the MNs, thereby more surface for Ag distribution and pesticide collection subsequently high sensitivity of the sensor [86]. The aforementioned data and Table 2 suggested that MNs-based sensing technologies emerged as newer technological solutions for pesticide detection in agriculture, especially real-time monitoring. Moreover, designing MNs significantly affects the sensitivity, selectivity, and stability towards pesticide detection due to increased active sites for sensing and collecting pesticide residue. In general, we can say that MNs-based technology significantly influences the productivity of crops as real-time monitoring of toxic elements.

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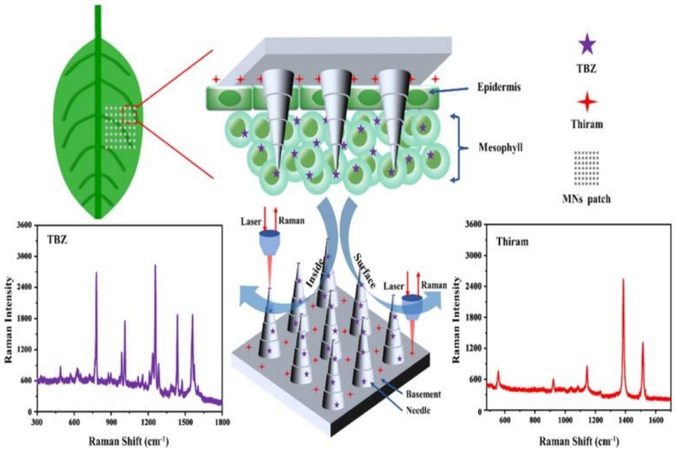

Fig. 5. A schematic representation of the pesticide residue in agricultural products using MNs. The image was reproduced with permission [86] from ACS, copyright @2023.

5.2. Redox status of fruits and vegetables

The redox status of fruits and vegetables is an indicator of oxidative/reductive molecules like redox couples, free radicals, enzymes, and the thiols group of protein. The balance of redox species includes reactive oxygen species (ROS) that maintain physiological function within the plants, whereas the imbalance of redox species leads to oxidative stress and cell death. Therefore, maintaining the balance of redox species is required to retain healthy plants. Unquestionably, fruits and vegetables are the main components in daily diets with numerous antioxidant molecules such as flavonoids, phenols, and vitamin C. Different fruits/vegetables have different antioxidant molecules, and the same fruits/vegetables also have different amounts of antioxidant molecules at different stages of growth/storage. However, antioxidant molecules are the main constraints for the estimation of fruits/vegetable's nutritional values and freshness [87-89]. In this aspect, it is necessary to detect redox species to understand the nutritional values and freshness of the fruits/vegetables. Few studies reported that the MNs-based sensor has been effectively

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used to detect redox species from fruits/vegetables. For instance, Dhanjai and Lu fabricated layer-by-layer assembly with CNTs-cellulose nanocrystals and polyaniline conductive polymer modified stainless steel (MSS) MSS-MNs-based electrodes for real-time monitoring of plant polyphenols such as chlorogenic acid (CA) and gallic acid (GA). The prepared MSS-MNs effectively detect GA and CA in orange. The data suggested that the MSS-MNs might be a potential sensing device to measure total antioxidant capacity in fruits [90]. In another study of the same research group, fabricated MSS-MNs integrated with a redox mediator system (MSS-MNs-RMS) for detecting fish spoilage, antioxidant molecules in mushrooms, and brew coffee samples. The data indicated that the MSS-MNs-RMS effectively detect redox species, including ABA, H_2O_2, and putrescine, with the detection limit of ~50, 80, and 263 ng/mL, respectively. Interestingly, portable, rapid, sensitive, and easy to apply in real-time monitoring [91]. Kim et al. fabricate bioink-incorporated silk fibroin-based porous MNs (BI-SF-MNs) to detect pathogens in the food supply. **Fig. 6** shows the graphical representation of the fabrication of BI-SF-MNs and their application. The data indicate that the BI-SF-MNs effectively detect the pathogen in the food supply by changing the pH. Interestingly, the color of the bioink changes from blue to red, clearly indicating the unhealthy food [92].

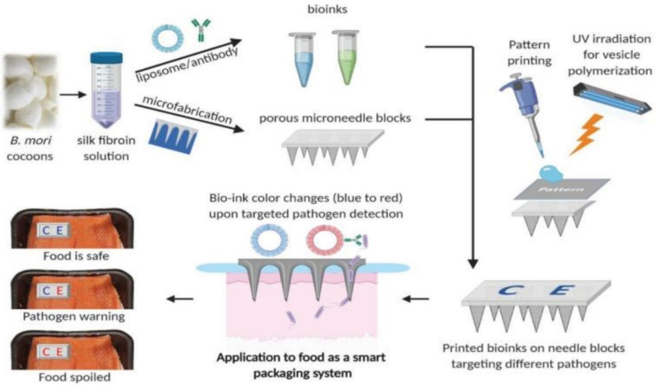

Fig. 6. A schematic illustration of the fabrication of BI-SF-MNs and their application. The image was reproduced with permission [92] from Wiley, copyright @2021.

Li et al. fabricated MNs onto the Au-nano shells substrate to develop a SERS-MNs-based sensor to detect the pH and redox status of the food sample. The data indicated that the SERS-MNs-based sensor effectively detects the pH and redox status of the fruits and vegetables [93]. The aforementioned studies and Table 1 suggested that the MNs-based sensor effectively detects the redox status of the fruits and vegetables with high sensitivity and stability. Moreover, MNs-based sensors prevent the extraction process and contact the atmospheric air. Furthermore, MNs-based sensors can penetrate anywhere in fruits/vegetables (solid/liquid tissues) to detect pH and redox species. The interferent effect in the MNs-based sensor might be minimized by employing several strategies including surface functional group, selective coatings, and incorporating enzymes to ensure accurate detection of analytes. We can say that the MNs-based sensing technology might offer a versatile platform to detect numerous indicators, including nutritional values, freshness, and redox species within the fruits/vegetables, without damaging the tissues.

Table. 2. Different MNs-based sensors for monitoring of food

S. N	**MNs-based sensor**	**Food/Plant**	**Analytes**	**Remarks**	**Ref**
1.	IMP-MNs	Honey	Imidacloprid	Effectively detect pesticides from food samples	83
2.	PVA-HA-MNs	Leave	Thiram & thiabendazole	MNs-based sensor detects Thiram and Thiabendazole with detection limits of 10^{-7} and 10^{-8} M, respectively.	[illegible]

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3.	Adhesive tape coated with Au-NPs	Apple, orange, cucumber	Parathion-methyl, thiram & chlorpyrifos	The paste and peel-oof approach-based sensor effectively detects pesticides.
4.	MNs	-	Organophosphates	The prepared sensor effectively detects pesticides as a wearable sensor.
5.	MSS-MNs	Orange	GA and CA	MSS-MNs might be potential sensing devices to measure the total antioxidant capacity in fruits.
6.	MSS-MNs-RMS	Fish spoilage, mushroom, and brew coffee samples.	ABA, H_2O_2, and putrescine	Effectively detects redox species and is easy to apply in real-time monitoring.
7.	SF-MNs	Food supply	Pathogens	Effectively detect pathogens and spoilage by increasing the pH condition.
8.	SERS-MNs	Fruits and Vegetables	pH and redox species	Effectively detect pH and redox species with high sensitivity.

6. Future perspectives

In recent years, the use of MNs and the interpretation of knowledge from human medicine have entered farming and flora wellbeing. To meet the challenges of the farming industry, innovation in planting and precision agriculture is necessary to increase crop production, rehabilitate plants against stress and disease, and improve crop stability. Recently, various MNs-based biosensing platforms have been developed. Some ideas need to be pursued for simpler and cheaper microfabrication techniques to create MNs using simpler materials. Advances in ultra-rapid prototyping procedures will permit the production of MNs. In addition, due to the combination of liquids in plants, the steadiness of MNs-based detectors after interaction with liquid should be evaluated. Thus, additional materials development for the synthesis of MNs is required in the upcoming period. This article presents the newest advances in MNs technology for illness recognition and flora monitoring. The MNs-based technology can potentially carry knowledge to agriculturalists and benefit them. This innovation allows many traditional chemical tests to be done more efficiently and quickly on crops, analyzing whole crops against pathogenic diseases that help in the prevention strategies. The upcoming era of smart farming biosensing depends on detectors' sensitivity, consistency, and specificity, with efficiency, low cost, and small components.

7. Conclusion

MNs can be divided into solid, coating, separation, and hydrogel preparation. MNs are fabricated using silicon, metal, polymers, glass, and ceramics. The MNs-based sensing device constantly monitors plant well-being and diagnoses of plant diseases. Although numerous MNs-based sensing devices have been reported for human health, diagnosis, and treatment, using this knowledge in farming has only just begun. The *in-vivo* and *in-vitro* MNs-based non-destructive sensing devices provide on-site information on plant health, thereby significantly improving crop productivity due to early treatment strategy to prevent disease. Moreover, MNs-based innovative solutions will support agriculture in many ways: (1) rapid development of precision agriculture, (2) enhancement the food quality by maintaining nutritional values, and (3) reduction of the loss of crops due to early treatment strategy to protect against pathogens and control the nutrients within the plants. Therefore, real-time monitoring of the crops significantly aided the advantage of monitoring plants at the initial stage of infection, thereby increasing the productivity of crops. It is important to mention that the non-enzymatic sensors have several challenges like selectivity and specificity. It seems difficult to detect specific analytes accurately with non-enzymatic sensors due to the presence of interfering substances. We need to take care of this limitation of non-enzymatic sensors to design MNs-based sensing technology in agriculture, especially in real-time monitoring of plant health. This prospective explores the latest developments in MNs-based sensing technology in food and health crops, including disease screening and diagnosis. Therefore, MNs-based sensing technology might accelerate plant surveillance and disease detection progress.

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References

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1. A. Raza, A. Razzaq, S. S. Mehmood, X. Zou, X. Zhang, Y. Lv and J. Xu, *Plants (Basel)*, 2019, **8**.
2. I. Egea, Y. Estrada, C. Faura, J. M. Egea-Fernández, M. C. Bolarin and F. B. Flores, *Front Plant Sci*, 2023, **14**, 1092885.
3. M. G. Muluneh, *Agriculture & Food Security*, 2021, **10**, 36.
4. S. C. Teixeira, N. O. Gomes, M. L. Calegaro, S. A. S. Machado, T. V. de Oliveira, N. de Fátima Ferreira Soares and P. A. Raymundo-Pereira, *Biomaterials Advances*, 2023, **155**, 213676.
5. R. T. Paschoalin, N. O. Gomes, G. F. Almeida, S. Bilatto, C. S. Farinas, S. A. S. Machado, L. H. C. Mattoso, O. N. Oliveira and P. A. Raymundo-Pereira, *Biosensors and Bioelectronics*, 2022, **199**, 113875.
6. M. Venbrux, S. Crauwels and H. Rediers, *Frontiers in Plant Science*, 2023, **14**.
7. D. M. Rizzo, M. Lichtveld, J. A. K. Mazet, E. Togami and S. A. Miller, *One Health Outlook*, 2021, **3**, 6.
8. M. Tudi, H. Daniel Ruan, L. Wang, J. Lyu, R. Sadler, D. Connell, C. Chu and D. T. Phung, *Int J Environ Res Public Health*, 2021, **18**.
9. B. K. Singh, M. Delgado-Baquerizo, E. Egidi, E. Guirado, J. E. Leach, H. Liu and P. Trivedi, *Nature Reviews Microbiology*, 2023, **21**, 640-656.
10. I. Buja, E. Sabella, A. G. Monteduro, M. S. Chiriacò, L. De Bellis, A. Luvisi and G. Maruccio, *Sensors (Basel)*, 2021, **21**.
11. M. J. Sue, S. K. Yeap, A. R. Omar and S. W. Tan, *Biomed Res Int*, 2014, **2014**, 653014.
12. S. Liu, K. Zhao, M. Huang, M. Zeng, Y. Deng, S. Li, H. Chen, W. Li and Z. Chen, *Frontiers in Bioengineering and Biotechnology*, 2022, **10**.
13. N. O. Gomes and P. A. Raymundo-Pereira, *Small*, 2023, **19**, 2206753.
14. N. O. Gomes, S. C. Teixeira, M. L. Calegaro, S. A. S. Machado, N. de Fátima Ferreira Soares, T. V. de Oliveira and P. A. Raymundo-Pereira, *Chemical Engineering Journal*, 2023, **472**, 144775.
15. S. C. Teixeira, N. O. Gomes, T. V. d. Oliveira, P. Fortes-Da-Silva, N. d. F. F. Soares and P. A. Raymundo-Pereira, *Biosensors and Bioelectronics: X*, 2023, **14**, 100371.
16. J. M. Roper, J. F. Garcia and H. Tsutsui, *ACS Omega*, 2021, **6**, 5101-5107.

View Article Online
DOI: 10.1039/D4MA00479E

17. M. C. Ang and T. T. S. Lew, *Front Plant Sci*, 2022, **13**, 884454.

18. K. Dyussembayev, P. Sambasivam, I. Bar, J. C. Brownlie, M. J. A. Shiddiky and R. Ford, *Frontiers in Chemistry*, 2021, **9**.

19. D. Trippa, R. Scalenghe, M. F. Basso, S. Panno, S. Davino, C. Morone, A. Giovino, S. Oufensou, N. Luchi, S. Yousefi and F. Martinelli, *Pest Management Science*, 2023, **n/a**.

20. M. Ashfaq, N. Verma and S. Khan, *Materials Chemistry and Physics*, 2018, **217**, 216-227.

21. R. A. Omar, S. Afreen, N. Talreja, D. Chauhan and M. Ashfaq, in *Plant Nanobionics: Volume 1, Advances in the Understanding of Nanomaterials Research and Applications*, ed. R. Prasad, Springer International Publishing, Cham, 2019, DOI: 10.1007/978-3-030-12496-0_6, pp. 117-140.

22. D. Chauhan, M. Ashfaq, R. V. Mangalaraja and N. Talreja, in *Nanomaterial Interactions with Plant Cellular Mechanisms and Macromolecules and Agricultural Implications*, eds. J. M. Al-Khayri, L. M. Alnaddaf and S. M. Jain, Springer International Publishing, Cham, 2023, DOI: 10.1007/978-3-031-20878-2_11, pp. 299-316.

23. M. A. Tahir, S. Hameed, A. Munawar, I. Amin, S. Mansoor, W. S. Khan and S. Z. Bajwa, *Journal of Virological Methods*, 2017, **249**, 130-136.

24. P. Zuo, X. Li, D. C. Dominguez and B. C. Ye, *Lab Chip*, 2013, **13**, 3921-3928.

25. F. Mahmood, S. S. Zehra, M. Hasan, A. Zafar, T. Tariq, H. U. Javed, X. Shu, H. Xue and M. Hatami, *Plant Physiology and Biochemistry*, 2023, **204**, 108081.

26. Q. Zhan, A. Ahmad, H. Arshad, B. Yang, S. K. Chaudhari, S. Batool, M. Hasan, G. Feng, G. Mustafa and M. Hatami, *Plant Physiol Biochem*, 2024, **211**, 108719.

27. P. A. Raymundo-Pereira, N. O. Gomes, F. M. Shimizu, S. A. S. Machado and O. N. Oliveira, *Chemical Engineering Journal*, 2021, **408**, 127279.

28. L. Tessaro, A. Aquino, P. Panzenhagen, A. C. Ochioni, Y. S. Mutz, P. A. Raymundo-Pereira, I. R. Vieira, N. K. Belem and C. A. Conte-Junior, *Journal*, 2022, **12**.

29. A. Aquino, V. M. F. Paschoalin, L. L. G. Tessaro, P. A. Raymundo-Pereira and C. A. Conte-Junior, *Journal of Pharmaceutical and Biomedical Analysis*, 2022, **211**, 114608.

30. X. Jin, D. D. Zhu, B. Z. Chen, M. Ashfaq and X. D. Guo, *Advanced Drug Delivery Reviews*, 2018, **127**, 119-137.

31. V. Alimardani, S. S. Abolmaali, A. M. Tamaddon and M. Ashfaq, *Drug Delivery and Translational Research*, 2021, **11**, 788-816.

32. B. Z. Chen, M. Ashfaq, D. D. Zhu, X. P. Zhang and X. D. Guo, *Macromolecular Rapid Communications*, 2018, **39**, 1800075.

33. J. N. Zhang, B. Z. Chen, M. Ashfaq, X. P. Zhang and X. D. Guo, *Journal of Industrial and Engineering Chemistry*, 2018, **65**, 363-369.

34. M. C. He, B. Z. Chen, M. Ashfaq and X. D. Guo, *Drug Delivery and Translational Research*, 2018, **8**, 1034-1042.

35. B. Z. Chen, Y. Yang, B. B. Wang, M. Ashfaq and X. D. Guo, *International Journal of Pharmaceutics*, 2019, **556**, 338-348.

36. P. Dardano, I. Rea and L. De Stefano, *Current Opinion in Electrochemistry*, 2019, **17**, 121-127.

37. J. J. García-Guzmán, C. Pérez-Ràfols, M. Cuartero and G. A. Crespo, *TrAC Trends in Analytical Chemistry*, 2021, **135**, 116148.

38. Y. Wu, F. Tehrani, H. Teymourian, J. Mack, A. Shaver, M. Reynoso, J. Kavner, N. Huang, A. Furmidge, A. Duvvuri, Y. Nie, L. M. Laffel, F. J. Doyle, III, M.-E. Patti, E. Dassau, J. Wang and N. Arroyo-Currás, *Analytical Chemistry*, 2022, **94**, 8335-8345.

39. Z. Faraji Rad, *Advanced Engineering Materials*, 2023, **25**, 2201194.

40. E. Ece, I. Eş and F. Inci, *Materials Today*, 2023, **68**, 275-297.

41. A. Bukhamsin, K. Moussi, R. Tao, G. Lubineau, I. Blilou, K. N. Salama and J. Kosel, *Adv Sci (Weinh)*, 2021, **8**, e2101261.

42. Z. Li, T. Yu, R. Paul, J. Fan, Y. Yang and Q. Wei, *Nanoscale Advances*, 2020, **2**, 3083-3094.

43. R. F. Donnelly, T. R. Raj Singh and A. D. Woolfson, *Drug Deliv*, 2010, **17**, 187-207.

44. T. M. Tuan-Mahmood, M. T. McCrudden, B. M. Torrisi, E. McAlister, M. J. Garland, T. R. Singh and R. F. Donnelly, *Eur J Pharm Sci*, 2013, **50**, 623-637.

45. D. Ramadon, M. T. C. McCrudden, A. J. Courtenay and R. F. Donnelly, *Drug Deliv Transl Res*, 2022, **12**, 758-791.

46. J. Yang, J. Yang, X. Gong, Y. Zheng, S. Yi, Y. Cheng, Y. Li, B. Liu, X. Xie, C. Yi and L. Jiang,

Advanced Healthcare Materials, 2022, **11**, 2102547.

47. Y. Cao, S. S. Koh, Y. Han, J. J. Tan, D. Kim, N. H. Chua, D. Urano and B. Marelli, *Adv Mater*, 2023, **35**, e2205794.
48. A. Kundu, M. G. Nogueira Campos, S. Santra and S. Rajaraman, *Sci Rep*, 2019, **9**, 14008.
49. S. Dugam, R. Tade, R. Dhole and S. Nangare, *Future Journal of Pharmaceutical Sciences*, 2021, **7**, 19.
50. Ö. Erdem, I. Eş, G. A. Akceoglu, Y. Saylan and F. Inci, *Journal*, 2021, **11**.
51. I. Eş, A. Kafadenk, M. B. Gormus and F. Inci, *Small*, 2023, **19**, 2206510.
52. N. Tariq, M. W. Ashraf and S. Tayyaba, *Journal of Pharmaceutical Innovation*, 2022, **17**, 1464-1483.
53. T. Waghule, G. Singhvi, S. K. Dubey, M. M. Pandey, G. Gupta, M. Singh and K. Dua, *Biomedicine & Pharmacotherapy*, 2019, **109**, 1249-1258.
54. R. S. J. Ingrole and H. S. Gill, *J Pharmacol Exp Ther*, 2019, **370**, 555-569.
55. H. S. Gill and M. R. Prausnitz, *J Control Release*, 2007, **117**, 227-237.
56. H. Du, P. Liu, J. Zhu, J. Lan, Y. Li, L. Zhang, J. Zhu and J. Tao, *ACS Applied Materials & Interfaces*, 2019, **11**, 43588-43598.
57. N. G. Oh, S. Y. Hwang and Y. H. Na, *ACS Omega*, 2022, **7**, 25179-25185.
58. L. Van Hileghem, S. Kushwaha, A. Piovesan, P. Verboven, B. Nicolaï, D. Reynaerts, F. Dal Dosso and J. Lammertyn, *Journal*, 2023, **14**.
59. M. Ashfaq, N. Verma and S. Khan, *Environmental Science: Nano*, 2017, **4**, 138-148.
60. R. Kumar, M. Ashfaq and N. Verma, *Journal of Materials Science*, 2018, **53**, 7150-7164.
61. S. Afreen, R. A. Omar, N. Talreja, D. Chauhan, R. V. Mangalaraja and M. Ashfaq, in *Copper Nanostructures: Next-Generation of Agrochemicals for Sustainable Agroecosystems*, ed. K. A. Abd-Elsalam, Elsevier, 2022, DOI: https://doi.org/10.1016/B978-0-12-823833-2.00004-0, pp. 367-391.
62. Z. Wang, L. Xue, M. Li, C. Li, P. Li and H. Li, *Materials Science and Engineering: C*, 2021, **127**, 112237.
63. R. Paul, E. Ostermann, Y. Chen, A. C. Saville, Y. Yang, Z. Gu, A. E. Whitfield, J. B. Ristaino and Q. Wei, *Biosensors and Bioelectronics*, 2021, **187**, 113312.
64. R. Omar, Y. Zheng, J. Wang and H. Haick, *Advanced Sensor Research*, 2023, **2**, 2200032.
65. S. Dutta, S. Pal, P. Panwar, R. K. Sharma and P. L. Bhutia, *ACS Omega*, 2022, **7**, 25909-25920.
66. B. Kashyap and R. Kumar, *Journal*, 2021, **6**.
67. T. T. S. Lew, R. Sarojam, I.-C. Jang, B. S. Park, N. I. Naqvi, M. H. Wong, G. P. Singh, R. J. Ram, O. Shoseyov, K. Saito, N.-H. Chua and M. S. Strano, *Nature Plants*, 2020, **6**, 1408-1417.
68. S. N. Daskalakis, G. Goussetis, S. D. Assimonis, M. M. Tentzeris and A. Georgiadis, *IEEE Sensors Journal*, 2018, **18**, 7889-7898.
69. E. Jeon, S. Choi, K.-H. Yeo, K. S. Park, M. L. Rathod and J. Lee, *Journal of Micromechanics and Microengineering*, 2017, **27**, 085009.
70. A. Bukhamsin, K. Moussi, N. Patel, A. Przybysz, Y. Wang, S. Krattinger and J. Kosel, 2020.
71. N. I. Hossain and S. Tabassum, 2022.
72. S. Baek, E. Jeon, K. S. Park, K. H. Yeo and J. Lee, *Journal of Microelectromechanical Systems*, 2018, **27**, 440-447.
73. Y. Acanda, S. Welker, V. Orbović and A. Levy, *Plant Cell Reports*, 2021, **40**, 1171-1179.
74. B. O. Flynn, M. D. Donno, C. Barrett, C. Robinson and A. O. Riordan, 2017.
75. S.-H. Cai, W. Chen, D. Di, Z.-C. Yuan, R. Jiang, W. Gao and B. Hu, *International Journal of Mass Spectrometry*, 2022, **473**, 116793.
76. C. Hegarty, A. McConville, R. J. McGlynn, D. Mariotti and J. Davis, *Materials Chemistry and Physics*, 2019, **227**, 340-346.
77. Y. Fang and R. P. Ramasamy, *Biosensors (Basel)*, 2015, **5**, 537-561.
78. R. Paul, A. C. Saville, J. C. Hansel, Y. Ye, C. Ball, A. Williams, X. Chang, G. Chen, Z. Gu, J. B. Ristaino and Q. Wei, *ACS Nano*, 2019, **13**, 6540-6549.
79. R. Paul, E. Ostermann and Q. Wei, in *Plant Pathology: Method and Protocols*, ed. N. Luchi, Springer US, New York, NY, 2022, DOI: 10.1007/978-1-0716-2517-0_4, pp. 77-90.
80. F. Arduini, S. Cinti, V. Scognamiglio and D. Moscone, *Microchimica Acta*, 2016, **183**, 2063-2083.
81. M.-L. Xu, Y. Gao, X. X. Han and B. Zhao, *Journal of Agricultural and Food Chemistry*, 2017, **65**, 6719-6726.
82. S. Sindhu and A. Manickavasagan, *Comprehensive Reviews in Food Science and Food Safety*, 2023, **22**, 1226-1256.

View Article Online
DOI: 10.1039/D4MA00479E

83. S. M. Mugo, W. Lu and S. V. Robertson, *Journal*, 2022, **22**.
84. J. Chen, Y. Huang, P. Kannan, L. Zhang, Z. Lin, J. Zhang, T. Chen and L. Guo, *Analytical Chemistry*, 2016, **88**, 2149-2155.
85. R. K. Mishra, A. M. Vinu Mohan, F. Soto, R. Chrostowski and J. Wang, *Analyst*, 2017, **142**, 918-924.
86. X. Yi, Z. Yuan, X. Yu, L. Zheng and C. Wang, *ACS Applied Materials & Interfaces*, 2023, **15**, 4873-4882.
87. B. D'Autréaux and M. B. Toledano, *Nature Reviews Molecular Cell Biology*, 2007, **8**, 813-824.
88. A. Mansouri, G. Embarek, E. Kokkalou and P. Kefalas, *Food Chemistry*, 2005, **89**, 411-420.
89. K. Thaipong, U. Boonprakob, K. Crosby, L. Cisneros-Zevallos and D. Hawkins Byrne, *Journal of Food Composition and Analysis*, 2006, **19**, 669-675.
90. Dhanjai, S. M. Mugo and W. Lu, *Analytical and Bioanalytical Chemistry*, 2020, **412**, 7063-7072.
91. S. M. Mugo, Dhanjai, W. Lu and S. Robertson, *Journal*, 2022, **12**.
92. D. Kim, Y. Cao, D. Mariappan, M. S. Bono Jr, A. J. Hart and B. Marelli, *Advanced Functional Materials*, 2021, **31**, 2005370.
93. Z. Li, C. Pan, J. Sun, W. Qian and J. Dong, *ACS Food Science & Technology*, 2021, **1**, 1787-1791.

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DOI: 10.1039/D4MA00479E

Data Availability statements

Data sharing is not applicable to this article as no datasets were generated or analysed during the current study.