Trends in Analytical Chemistry 191 (2025) 118336

Contents lists available at ScienceDirect

Trends in Analytical Chemistry

journal homepage: www.elsevier.com/locate/trac

Recent advances in wearable and implantable electrochemical (bio)sensors for plant health monitoring

Narjiss Seddaoui, Fabiana Arduini *

Department of Chemical Science and Technologies, University of Rome "Tor Vergata", Via Della Ricerca Scientifica, 00133, Rome, Italy

ARTICLE INFO

Keywords:
Internet of plants
Plant (bio)sensors
Wearable devices
Implantable devices
Electrochemical transduction
Nanotechnology

ABSTRACT

In 2023, the World Economic Forum selected wearable plant sensors as one of the Top 10 Emerging Technologies, demonstrating that these smart analytical tools will be relevant in the next generation of agrifood practices. Considering the robustness, accuracy, and miniaturisation of electrochemical (bio)sensing tools, electrochemical-based plant sensors could be suitable devices to address the requirements for their advanced applications in the agrifood sector. This review deals with electrochemical (bio)sensors for monitoring agrochemicals, phytohormones, growth precursors, and stress biomarkers, using wearable and implantable configurations. The design and type of biocomponent and/or nanomaterial(s) used are reported, highlighting the analytical performances obtained on plants. The ongoing application of these analytical tools is discussed, and the future applications combined with Internet of Thing and Artificial Intelligence are envisioned, with the overriding aim to give an overall scenario related to plant electrochemical (bio)sensors for the next technologies in the agrifood sector.

1. Introduction

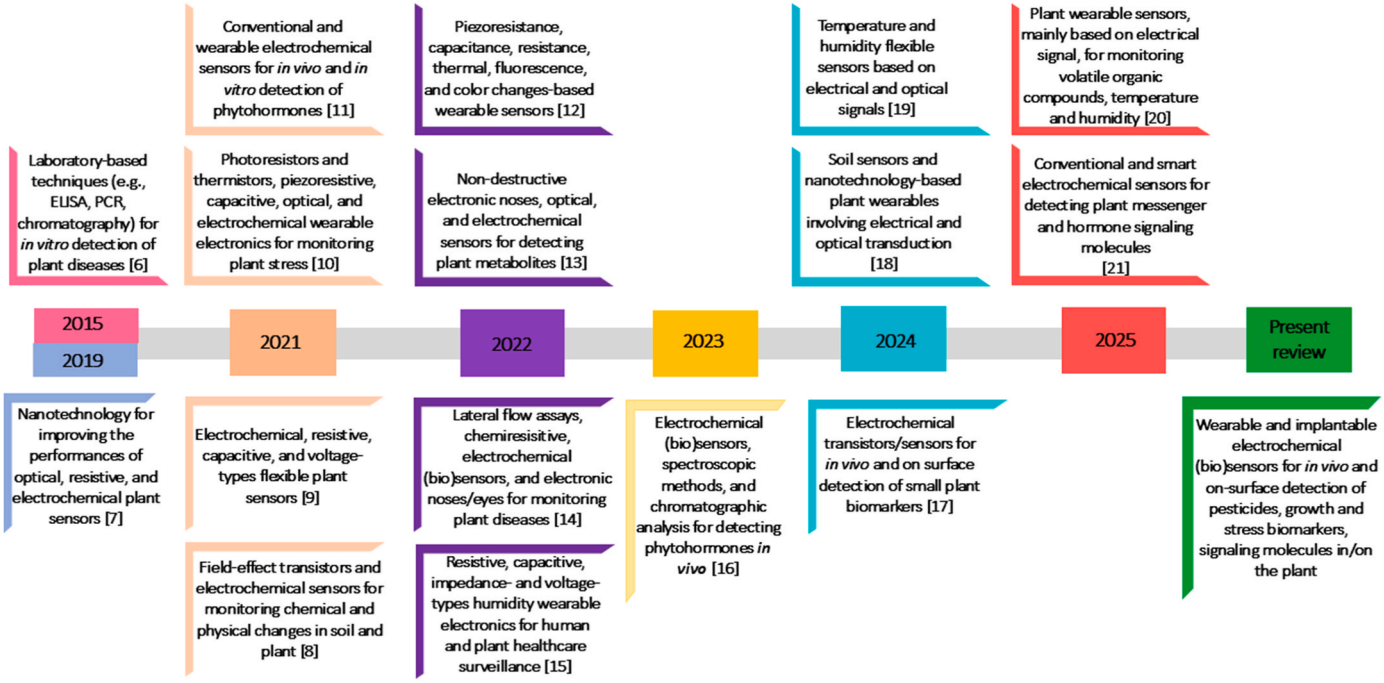
Wearable and implantable sensors have become increasingly popular for biomedical applications due to their portability and ability to perform on-site, non-invasive, and real-time analysis at the point-of-care [1]. The ongoing progress of the Internet of Things (IoT) has expanded the use of wearable sensors in the biomedical field [2,3] and beyond medical applications. Today, a new concept known as the Internet of Plants (IoP) has emerged. The idea is to equip plants with sensors capable of collecting and transmitting data related to their chemical, physical, physiological, and environmental needs [4]. The relevance of wearable plant sensors has been recently highlighted by the World Economic Forum, which reported in June 2023 that wearable plant sensors are among the Top 10 Emerging Technologies of 2023 [5].

This important recognition of these smart devices is ascribed to their potential capability to revolutionise crop production and management. In the era of precision agriculture, wearable and implantable plant sensors are crucial for assisting and boosting precision agriculture. In detail, sensors are considered wearable when mounted on plants, such as on leaves and stems, while implantable ones are inserted directly into the stem or inside the plant's fruit. The in-situ monitoring of plant key analytes, the *in vivo* determination of molecules circulating within the plant's vascular system (xylem/phloem), and the detection of volatile compounds emitted by plant stomata under different conditions using smart sensors will ensure sample integrity and high reliability giving an added value when compared to classical sampling methods. Furthermore, wearable and implantable sensors are non-destructive or minimally invasive, suitable for various parts of plants such as stems and leaves, where intimate contact between the plant and the sensor is ensured. In this way, the use of plant sensors to study plant physiological metabolism and plant response to environmental stress (biotic and abiotic) will better comprehend plant growth phenomena, with a huge impact on the future of agrifood practices.

The scientific community has shown significant interest in plant analytical tools, leading to a growing number of reviews in this field [6–21], starting from the laboratory-setup methods [6], through the interesting review by Giraldo et al. [7], which highlighted the importance of nanobiotechnology for smart plant sensors, up to several optical, piezoresistive, capacitive, and electrochemical sensors [8–21]. As summarised in Scheme 1, most reported reviews focus on type analytical techniques, with a cursory glance at wearable and implantable plant sensors. Moreover, some reviews that describe electrochemical (bio) sensors do not encompass a wide range of plant biomarkers and contaminants and present classical bio(sensors) and laboratory-based

* Corresponding author.
E-mail address: fabiana.arduini@uniroma2.it (F. Arduini).

https://doi.org/10.1016/j.trac.2025.118336
Received 8 June 2025; Accepted 8 June 2025
Available online 9 June 2025



Scheme 1. Summary of published reviews dealing with the detection of plant molecules using *in vitro* and *in vivo* analytical methods.

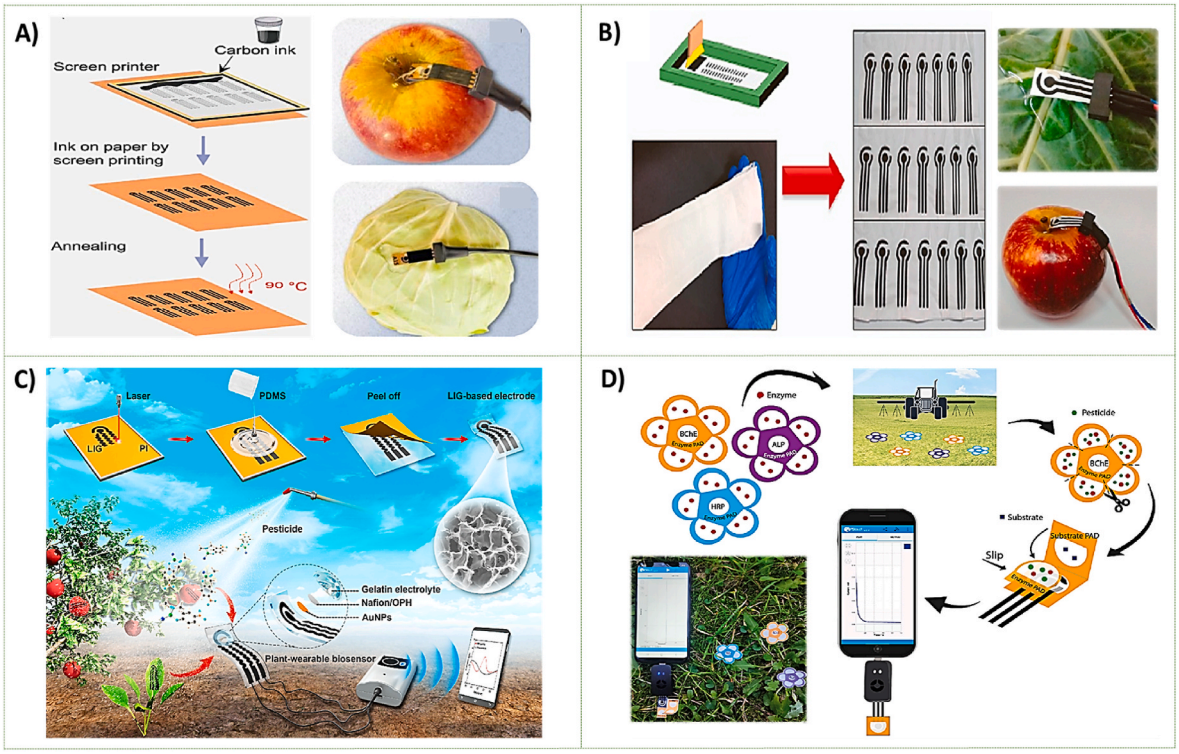


Fig. 1. Wearable electrochemical (bio)sensors constructed on A) kraft paper. Reprinted with permission from Ref. [22], B) poly(lactic acid) mats. Reprinted with permission from Ref. [23], C) Polyimide film and PDMS polymer. Reprinted with permission from Ref. [25], and D) office paper. Reprinted with permission from Ref. [27], for the detection of pesticides in liquid and aerosol phases.

methods.

This review is distinguished from previous ones in two significant ways. Firstly, it focuses exclusively on electrochemical analysis, providing a thorough discussion of both wearable and implantable configurations for *in vivo* monitoring of plant health. Conventional analytical methods and (bio)sensors developed for the ex-situ analysis of plant molecules are not covered. Secondly, the present review is the first to encompass all the plant molecules and related signals that have been monitored to date using wearable and implantable electrochemical (bio) sensors. These include stress biomarkers, growth biomarkers, signaling molecules, agrochemicals, volatile compounds, and other plant metabolites. In detail, this review draws a clear distinction between the

wearable and implantable electrochemical (bio)sensors developed to date for monitoring plant molecules. The design, construction, and analytical performances of each (bio)sensor are examined in depth to provide an overall understanding of the sensing mechanism. The use of sustainable materials, bioreceptors, and nanomaterials in fabricating these (bio)sensors is described, considering the advantages and disadvantages of each configuration. Additionally, the use of wearable and implantable (bio)sensors in precision agriculture is examined, thereby highlighting the considerable potential of this novel technology, as well as the deficiencies of these (bio)sensors, which necessitate significant refinement.

2. Wearable and implantable electrochemical (bio)sensors for plant health surveillance

2.1. Agrochemicals

2.1.1. Wearable (bio)sensors

Recently, plant wearable sensors have shown a great application in detecting pesticides. For instance, electrochemical sensors have been developed to detect carbendazim, a broad-spectrum carbamate fungicide that presents mutagenic and reprotoxic effects. To assess the misuse of this pesticide, sensors constructed on kraft and parchment paper substrates were developed to monitor the presence of carbendazim on the skin of apples and cabbages in real-time [22]. As shown in Fig. 1A, a complete electrochemical cell with counter, working, and reference electrodes was fabricated on paper substrates, using screen-printing technology, and placed on the surface of apples and cabbages. The detection of carbendazim was achieved by connecting the printed electrochemical sensor to a potentiostat through a connector adapted to the surface of the fruit and vegetables. The morphological and electrochemical characterisation of parchment and kraft papers revealed that the latter has significant potential for detecting carbendazim due to its porous nature, which allows for a large electrode surface area and the formation of a high number of carboxylic groups on the paper surface during electrochemical activation in acidic media. To simulate real-world applications, 100 μM of carbendazim solution was sprayed on apples and cabbages, dried at room temperature, and dissolved on both samples' skin using phosphate buffer. The concentrations of carbendazim found on the surface of the samples ranged from 0.7 μM to 1.1 μM for apples and from 0.3 μM to 1.3 μM for cabbage, by monitoring the oxidation of carbendazim at + 0.57 V on kraft paper-based sensor, using differential pulse voltammetry (DPV). The applicability of the developed sensor in detecting carbendazim in the presence of possible agrochemicals such as glyphosate, paraquat, thiram, diquat, and fenitrothion was assessed as well, showing no increase in the anodic current peak after adding the selected interferents, confirming the specificity of the developed wearable sensors. In addition, the developed sensor showed great mechanical stability with only an 8 % reduction after 100 cycles.

To offer a more sustainable, biocompatible, and highly flexible wearable sensor that can be mounted on irregular, wavy, and curved surfaces of crops, mats of poly(lactic acid) (PLA) were prepared via solution blow spinning procedure and used to print a complete electrochemical sensor, through screen-printing technology, as shown in Fig. 1B. Thanks to the high flexibility of PLA, sensors were placed on the skin of apple and cabbage and used for the individual detection of carbendazim and diquat by monitoring their oxidation at + 0.57 V and - 0.7 V using DPV and square wave voltammetry (SWV), respectively [23]. Here again, the surface of fruit and vegetable samples was deliberately sprayed with 100 μM of pesticide solution (carbendazim or diquat) before analysis, allowing for the determination of 1.1 μM and 0.38 μM of carbendazim, and 0.32 μM and 0.97 μM of diquat, on the apple and cabbage skin, respectively. The reproducibility of PLA sensors was assessed in the presence of carbendazim solution, resulting in a relative standard deviation (RSD) equal to 9.5 % using four different sensors.

Another biocompatible and sustainable material is cellulose acetate biopolymer, which has recently been used to manufacture a flexible and fully printed non-enzymatic electrochemical sensor [24]. The sensor attached to the surface of lettuce and tomato plants with tape was used to detect carbendazim and paraquat. Following the same procedure described above, 1000 μM of carbendazim (or paraquat) solution was sprayed on crop skin, followed by monitoring the oxidation peak of carbendazim or paraquat at + 0.55 V and - 0.87 V using DPV and SWV, respectively. The selectivity of the sensors was studied *in vitro,* showing a negligible effect of the interferents (ascorbic acid, dopamine, estradiol, fenitrothion, linuron, methyl parathion, nitrate, and paracetamol) on the current signals with a slight fluctuation between 2 % and 16 % for carbendazim, and 9 % for paraquat. In this study, the flexibility of the sensors was investigated by conducting a series of bending deformations on the cellulose acetate substrate, demonstrating no significant difference in the voltammetric responses compared to undeformed devices, confirming their applicability to different plant surfaces.

In addition to the electrochemical sensors, which are frequently based on the direct oxidation of pesticides, the concentration of these chemicals sprayed onto crop surfaces can also be determined using wearable enzymatic biosensors. In such configurations, a specific enzyme can catalyse the hydrolysis of the analyte to an electroactive product. For instance, organophosphorus hydrolase enzyme and gold nanoparticles were used to modify the working electrode of a 3D porous laser-induced graphene (LIG)-based serpentine, which was fabricated on commercial polyimide film by a direct writing strategy [25]. To ensure the high flexibility of the biosensor and thus its adaptation to irregular crop surfaces, the serpentine was transferred to polydimethylsiloxane (PDMS) silicon polymer, as shown in Fig. 1C. By pasting the biosensor equipped with gelatin semisolid electrolyte on the leaf of spinach and fruit of apple, 100 μM of methyl parathion pesticide, previously sprayed on the samples, was hydrolysed, releasing *p*-nitrophenol that was monitored at around - 0.10 V using SWV.

However, the electrochemical signal obtained in the cases of the biosensors attached to the leaf of spinach and the apple fruit was significantly lower than that recorded with the biosensors attached to a piece of polyethylene terephthalate. This lack of sensitivity may be attributed to the complicated surface of agricultural products. These findings remain encouraging as the use of a thermostable enzyme (i.e., organophosphorus hydrolase) enhances the biosensor's storage stability, which is often the feature that hinders the on-site application. In this way, the biosensors can be used to monitor pesticide residues on crop surfaces, thereby advancing precision agriculture and ensuring food safety.

Once more, laser direct writing technology was utilised to construct a microfluidic biosensor, composed of LIG-Au electrodes and hydrophilic PDMS micro-channels, to be placed on plant leaves to detect methyl parathion insecticide [26]. The PDMS channels were equipped with suction ports to guarantee the continuous absorption of electrolyte under capillary action. Consequently, the insecticide is directed towards the electrode surface, where it undergoes hydrolysis due to the action of lipase, resulting in the generation of *para*-nitrophenol. This, in turn, leads to the formation of a redox probe. The placement of the biosensor on a leaf previously exposed to a methyl parathion solution resulted in a detection limit of 0.000646 μM in the linear range of 0.001 μM–2 μM, as evidenced by the DPV measurements. The analysis of plant samples was conducted by placing the biosensor on the leaves of *Epipremnum aureum* and lettuce. The leaves were cleaned, sprayed with the insecticide solution, and allowed to dry. They were subsequently sprayed with a phosphate buffer, leading to recovery values ranging from 94.30 to 99.84 %. Despite the non-invasiveness and the satisfactory analytical performance of the biosensor in terms of sensitivity, selectivity, and stability, it is imperative to clean the microchannels after each test to obtain accurate results. In addition, a decrease in sensitivity was observed at elevated concentrations (2–200 μM) of methyl parathion, which may be attributed to the accumulation of by-products on the electrode surface.

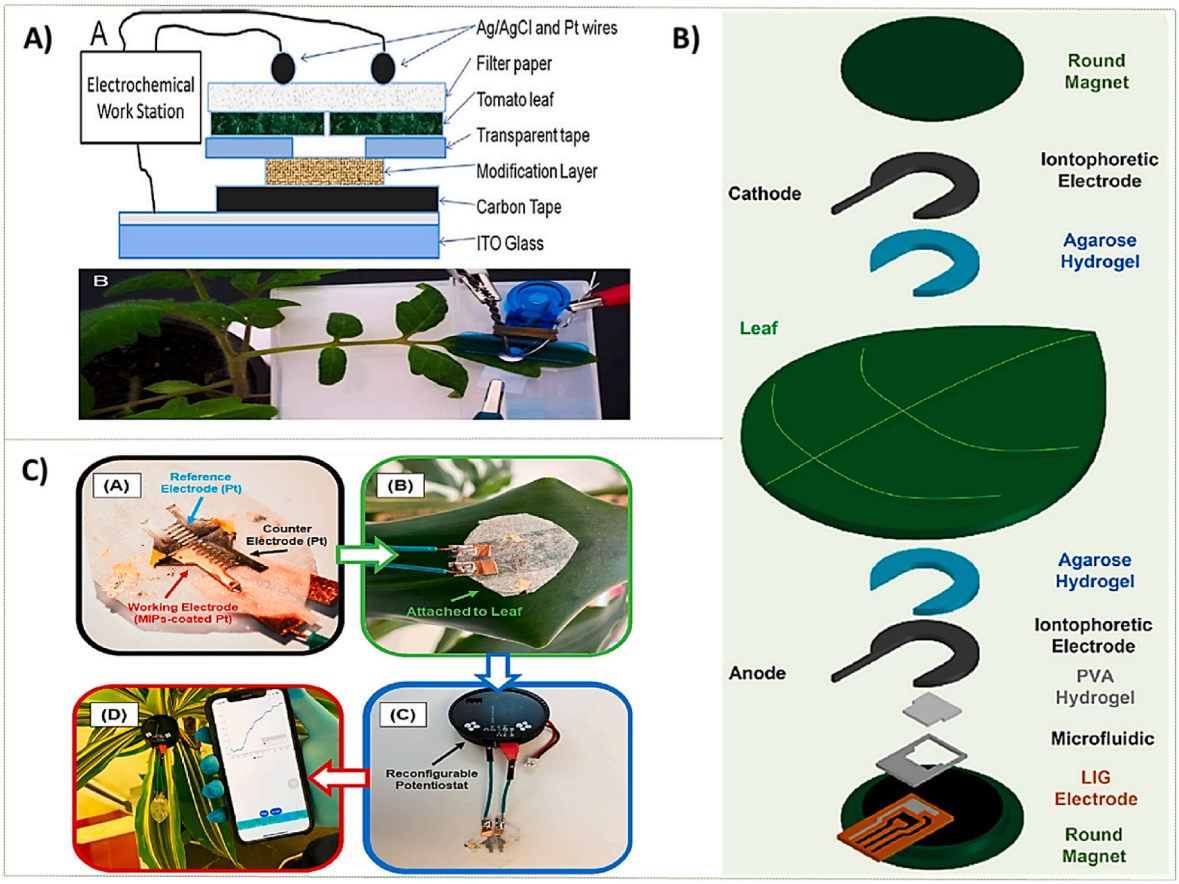


Fig. 2. A) A wearable electrochemical sensor made of carbon tape and filter paper for *in vivo* detection of salicylic acid in tomato leaves. Reprinted with permission from Ref. [28], B) A wearable non-destructive laser-induced graphene sensor for real-time detection of salicylic acid. Reprinted with permission from Ref. [29], C) A microneedle-based wearable biosensor combined with molecularly imprinted polymer for monitoring fungal infestation in Tobacco. Reprinted with permission from Ref. [31].

Beyond the wearable enzymatic biosensors applied to vegetables and fruit, we have designed a wearable biosensor for customising the use of pesticides in the agrifood practice, measuring the amount of pesticides in the soil. The idea was to create flower-like paper-based biosensors to be placed on the surface of the grass for analysing the excess use of pesticides that can reach the soil in the aerosol phase, being able to contaminate the soil and pollute the aquifer by water percolation. We demonstrated the reliability of this paper-based device by measuring paraoxon, 2,4-dichlorophenoxyacetic acid, and glyphosate pesticides, harnessing their inhibitory activity towards butyrylcholinesterase, alkaline phosphatase, and peroxidase, respectively [27]. We used office paper as a biocompatible and inexpensive substrate to print a complete electrochemical biosensor, whereas a flower-like pad with five petals was prepared using filter paper, preloaded with individual enzymes, and placed on grass before spraying the pesticide, as illustrated in Fig. 1D. The porosity of the paper of the flower-like system was used for sampling the pesticide in the aerosol phase, without any additional sampling system. For the pesticide quantification, each paper-based screen--printed electrodes were coupled to an enzyme pad and substrate pad in an origami format to monitor the activity of each enzyme after exposure to the corresponding pesticide. The biosensor was connected to a smartphone-assisted potentiostat, and the determination of the pesticide concentration began once the pesticide-enzyme pad was slid into the origami paper-based biosensor. According to the chronoamperometric measurements, the biosensors were able to detect 30 ppb, 10 ppb, and 2 ppb of 2,4-dichlorophenoxyacetic acid, glyphosate, and paraoxon, respectively, in the aerosol phase.

2.2. Phytohormones

2.2.1. Wearable (bio)sensors

Plant hormones are secondary metabolites that plants produce to regulate their growth, reproductive processes, longevity, and senescence. Among them, salicylic acid is known for acting as a signaling molecule for plant immunity against various biotic and abiotic stresses. Sun et al. developed a wearable carbon tape-based electrochemical sensor coated with multi-walled carbon tubes (MWCNTs) and Nafion for *in vivo* salicylic acid measurement [28]. The working layer was fixed on a conductive surface of indium tin oxide glass and used to sandwich the tomato leaf with Whatman filter paper used to i) store the buffer solution required to perform the assay and ii) provide a conductive connection between the three-electrode system as shown in Fig. 2A. To continuously monitor salicylic acid without affecting tomato growth, a small hole (⌀ = 1.5 mm) was made in the tomato leaf, allowing salicylic acid to diffuse onto the carbon tape-modified electrode and, therefore, its oxidation at + 0.7 V *vs* Ag/AgCl. The electrochemical sensing of salicylic acid in buffered solutions resulted in a limit of detection less than 0.05 μM and a RSD equal to 17 %, using the MWCNTs/Nafion-modified carbon tape electrodes. Herein, the reference and counter electrodes were reusable, thereby reducing the production cost of this electrochemical sensor. On the other hand, the real application of the wearable sensor was investigated in normal, phytoene desaturase (PDS) gene-silent, and diseased tomato leaves, showing a significant increase of salicylic acid concentration in diseased tomato leaves and plants under biotic stress.

Another sandwich configuration for monitoring salicylic acid content in plant leaves was fabricated by incorporating a reverse

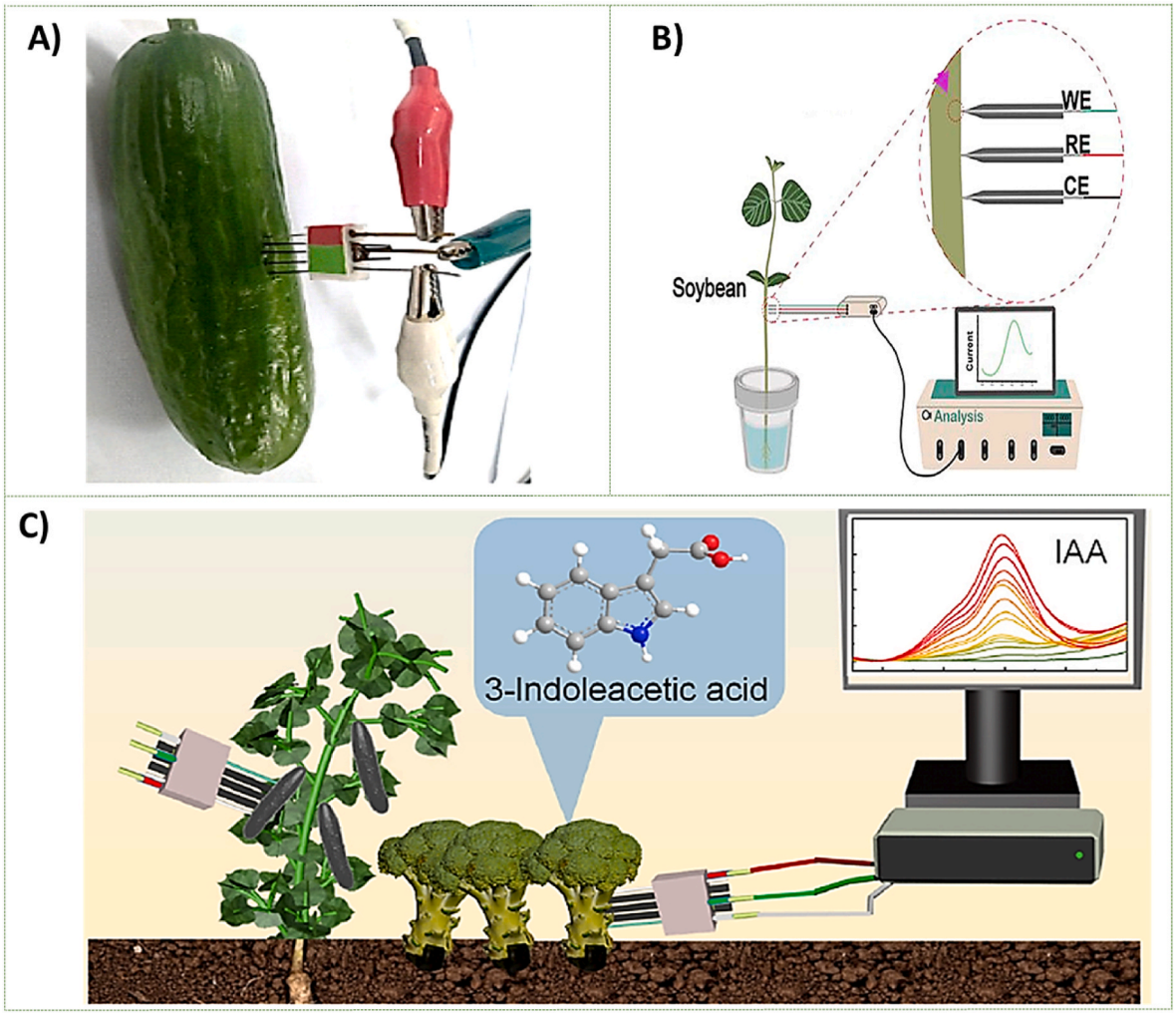


Fig. 3. A) A graphene-based microneedle implantable sensor for *in vivo* determination of abscisic acid in plants. Reprinted with permission from Ref. [32], B) A stainless steel-based implantable electrochemical microsensor for *in vivo* determination of indole-3-acetic acid in soybean seedlings. Reprinted with permission from Ref. [33], C) A vertical/horizontal graphene-based microneedle implantable microsensor for on-site detection of indole-3-acetic acid in cucumber and cauliflower. Reprinted with permission from Ref. [34].

iontophoretic system, capable of extracting liquid samples from leaves in a non-invasive manner, with LIG electrodes [29]. As illustrated in Fig. 2B, the sensor was attached to the leaf surface using two magnets, which serve as the anode and cathode terminals for the iontophoretic system. The anode magnet is responsible for holding i) the LIG electrodes, which facilitate the analyte oxidation, ii) a silver electrode that is used to apply the iontophoresis current, iii) an agarose hydrogel that serves as the electrical interface between the iontophoresis electrode and the plant leaf surface, and iv) a polyvinyl alcohol hydrogel that facilitates the diffusion of the extracted analyte across the electrodes. The configuration was closed by equipping the cathode magnet with an iontophoretic silver electrode and an agarose hydrogel. The *in vitro* study of the sensor in the presence of standard solutions of salicylic acid yielded a detection limit of 8.2 μM in the linear range comprised between 10 and 1000 μM, as measured by chronoamperometry at + 0.8 V. Furthermore, minimal interference in the presence of four metabolites (i.e. sucrose, fructose, oxalic acid, and citric acid) was observed.

In contrast, the *in vivo* application of the developed system was assessed by subjecting avocado plants to drought and salinity stresses over 10 days. The sensor was positioned on the plant leaf, and its response was stabilised by conducting 20 chronoamperometric scans. The extraction of salicylic acid from the leaves was achieved by applying a current magnitude of 0.53 mA for 10 min under chronopotentiometric mode. Finally, the electrochemical analysis of salicylic acid was performed with a constant oxidation potential of 0.8 V applied for 30 s, a sampling time interval of 0.2 s, and an equilibration time of 1 s. The *in vivo* studies demonstrated that the accumulation of endogenous salicylic acid was more pronounced in the case of drought stress. The findings confirm the vital role of water in plant growth and the rapid impact of its deficit on the avocado plant, in comparison to salinity stress, which is typically a long-term stressor.

In another design, an interdigitated microelectrode (IDME) array electrochemical sensor was constructed on a quartz substrate, with three groups of IDME arrays acting as a three-electrode system, for the *in vivo* monitoring of salicylic acid in cucumber [30]. The sensing area includes over 2000 microelectrodes, with a width of 1 μm each, which improved the mass transfer of the steady-state analyte by radial diffusion. To enhance the electrocatalytic activity of the sensor, core-shell Au@Cu_2O-graphene-polydopamine nanoparticles were densely packed onto the microelectrodes allowing the oxidation of salicylic acid at + 0.3 V. Before any practical application, 6 μL of salicylic acid solution with varying concentrations was applied to the sensor, resulting in a limit of detection equal to 1.16 nM within the analytical range of 0.01–100 μM and a RSD of 4.89 % across six sensors. The selectivity of the developed sensor towards salicylic acid was evaluated by measuring its peak current fluctuations in the presence of different molecules,

including indole-3-acetic acid, a phytohormone. The findings revealed a considerable interference, with a 12.6 % fluctuation in the peak current of salicylic acid in the presence of indole-3-acetic acid, in comparison to a 5 % change in the presence of other interfering molecules, highlighting the potential for indole-3-acetic acid to impede the detection of salicylic acid. To monitor the level of salicylic acid during plant growth, the sensor was mounted on living cucumber stems and leaves, showing a gradual increase in salicylic acid concentration over time. Specifically, the concentration ranged from 10.263 to 16.052 μM in the stems and from 0.107 to 0.688 μM in the leaves, indicating that the level of this phytohormone in the cucumber changes during its growth cycle. While the sensor holds great promise for real-time applications, its construction on a quartz substrate within a flat structure may not be suitable for monitoring salicylic acid on curved and irregular surfaces.

To cope with interference issues, a selective magnetic molecularly imprinted polymer (MIP) was combined with microneedles-based electrodes for *in vivo* applications [31]. As shown in Fig. 2C, the device incorporated combs of interdigitated electrodes decorated with conical microneedles. Once the microneedles have penetrated the cuticle and established contact with the leaf mesophyll, MIP can bind salicylic acid selectively in the apoplast, allowing its oxidation using chronoamperometric measurements conducted by a lightweight portable potentiostat obviating thigmomorphogenesis phenomena in the plant. *In vitro* studies of the prepared biosensor indicated a detection limit of 2.74 μM within a detection range of up to 150 μM. Furthermore, the selectivity of the biosensor was confirmed through the absence of electrochemical peaks for all phytohormones studied, including indole-3-acetic acid, at a concentration of 100 μM. The results indicate that the use of the biosensor for *in vivo* applications is unlikely to be constrained by the varying expression levels of other phytohormones. To evaluate the biosensor's response to pathogens infections in real applications, it was attached to healthy and *Botrytis cinerea* inoculated tobacco leaves of the same age, showing that the basal salicylic acid levels of the infected leaves increased 5 min after the inoculation, before the visible formation of spore lesions on the leaf. These findings suggest that the developed biosensor may be suitable for the early detection of fungal pathogens before visible lesions appear on leaves. The robust nature of the microneedles and the tight association between the magnetic electrodes and the polymers allowed for the reuse of the biosensor in a field setting, especially with the use of a portable reconfigurable potentiostat. Furthermore, the integration of MIP can be extended to other plant biomarkers through the preparation of magnetic MIPs imprinted with different templates.

2.2.2. Implantable sensors

Given the pivotal role of phytohormones in regulating plant growth and the persisting difficulties associated with the reliability of wearable sensors for ensuring consistent performance in fluctuating environmental conditions, researchers have turned to implantable sensors that can be directly inserted into plant tissues for *in vivo* detection of phytohormones.

In this regard, microneedles were used to construct an array sensor based on Au@SnO_2-vertical graphene (VG) grown on tantalum microelectrodes using a direct current arc plasma jet chemical vapor deposition method. Although the preparation of Au@SnO_2-VG microelectrodes is cumbersome, they present a low rate of invasion and a high capability to reach vasculature inside the plants, offering the possibility of *in vivo* monitoring of abscisic acid in cucumber fruit [32]. The final electrochemical configuration obtained by packing into a microneedle array three Au@SnO_2-VG microelectrodes, a platinum wire, and a titanium wire being the working, counter, and reference electrodes, respectively, showed great storage stability for at least 6 weeks. In addition, the VG film attributes high conductivity to the electrochemical system and serves as a carrier for Au@SnO_2 nanoparticles responsible for the direct oxidation of abscisic acid at + 1.25 V. By inserting the sensor inside the cucumber fruit, as demonstrated in Fig. 3A, the concentrations of abscisic acid in different cucumber fruits ranged between 0.087 μM and 95.17 μM, compared to 71.72 μM and 90.91 μM in cucumber juice. The considerable variation in abscisic acid concentration was attributed to the ability of the microneedle array sensor to measure the phytohormone in a localised area of the cucumber fruit, which in turn does not present the actual concentration of that phytohormone in the cucumber fruit. It is also important to note that the use of this sensor design may not be appropriate for all plant species, especially those with a rigid structure that may hinder the insertion of the microsensor.

Implantable sensors can also be conceived using stainless steel (SS) wires, which possess good electrical conductivity, high mechanical strength, and stable performance. In this regard, an anodised SS microelectrode was decorated with electrodeposited popcorn-like Au nanostructures, platinum nanoparticles, reduced graphene oxide nanocomposite films, and safranine T film to detect indole-3-acetic acid in soybean stem under salt stress, using two untreated SS wires as reference and counter electrodes [33]. By monitoring the oxidation peak of indole-3-acetic acid at + 0.7 V using DPV, the microsensor displayed good selectivity and great stability over 3 weeks, with limits of detection and quantification equal to 43 pg mL^{-1} and 143 pg mL^{-1}, respectively. The RSD was 7 % for 12 different microsensors in the presence of 100 μg mL^{-1} indole-3-acetic acid.

In vivo analysis of indole-3-acetic acid under salinity stress was conducted by inserting the sensor into the stems of soybean seedlings, as shown in Fig. 3B. Accordingly, the response of the microsensor varied as a function of salt concentrations and exposition time, as the concentration of indole-3-acetic acid increased up to 157.44 ± 23.03 ng mL^{-1} after 12 h of salt treatment and declined to 10.55 ± 2.84 ng mL^{-1} after 24 h. These findings confirm that the developed sensor can be used for *in vivo* evaluation of the abiotic effect of salt on soybean seedlings' growth. However, to maintain the integrity of both the microsensor and the plant, as well as to ensure continuous monitoring of the level of indole-3-acetic acid in the stem, it is imperative to avoid any contact between the microsensor and the plant tissue.

The detection of indole-3-acetic acid in vegetables was also reported using an implantable microneedle array sensor made of three vertical/horizontal graphene working microelectrodes (WE), combined with platinum (Pt) and titanium (Ti) wires as the counter and the reference electrodes, respectively [34]. The process of synthesising vertical graphene nanosheets on horizontal graphene layers, grown on a flat tantalum strip substrate, involved the utilisation of an electron-assisted hot-filament chemical vapor deposition method. The combination of different layers of graphene helps in increasing the contact area of the electrolyte, thereby improving the adsorption/desorption rate of the analyte and ensuring its enrichment and electrochemical oxidation.

By monitoring the oxidation of the analyte at around +0.7 V using DPV, it was found that the electrochemical performance of the sensor in standard solutions depends on the number of WE involved. Consequently, the sensitivity of the sensor with three WEs was found to be significantly higher than that of the sensors with one or two WEs. Furthermore, the limit of detection range of one-WE sensors was found to be approximately 0.30–0.71 μM, that of two-WE sensors was approximately 0.30–0.44 μM, and that of the three-WE sensor was approximately 0.21 μM. Moreover, the selectivity of the sensor was assessed in the presence of 20 interfering species, resulting in a fluctuation range of the analyte peak current between 0.27 % and 9.45 %.

Analysis of the vegetable samples was carried out by inserting the three-WE needle sensor into the cucumber and the root/stem connection of the cauliflower, as illustrated in Fig. 3C. However, analysis of six samples of each vegetable, performed five times in parallel, revealed a marked variation in the concentration of indole-3-acetic acid, ranging from 2.0 to 11.4 μM and from 1.7 to 4.8 μM, in the case of cucumbers and cauliflowers, respectively. Even though the microelectrodes prepared in the present work have a flat morphology that allows them to be attached to plant leaves or inserted into plant tissues (e.g. stems and roots), further efforts are still required to solve the problem of the

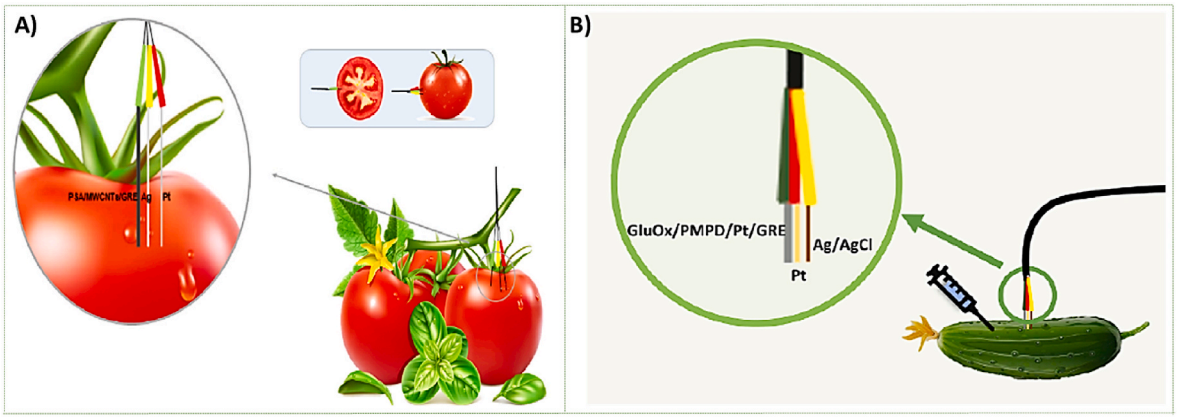


Fig. 4. A) An implantable miniaturised electrochemical sensor based on graphite rod electrode modified with multiwalled carbon nanotubes and poly(sulfosalicylic acid) film for *in vivo* detection of tryptophan in tomato fruits. Reprinted with permission from Ref. [36], B) An implantable enzymatic sensor modified with platinum nanoparticles and poly(*m*-phenylenediamine) film for the detection of glutamate in cucumber fruit. Reprinted with permission from Ref. [37].

accuracy of results, due to the presence of a high error value in real applications.

2.3. Growth precursors

2.3.1. Implantable (bio)sensors

The biosynthesis of the phytohormones mentioned above is generally controlled by growth precursor molecules such as tryptophan, which is an essential amino acid involved in the biosynthesis of the indole-3-acetic acid phytohormone. Furthermore, tryptophan can covalently bind to abscisic acid, responsible for inhibiting plant cell division under abiotic stress, which in turn promotes plant growth. The initial endeavour to monitor tryptophan in plants *in vivo* was accomplished by utilising a standard glassy carbon electrode (GCE) (dimensions: 10 mm × 20 mm x 1 mm) that was directly inserted into the tomato fruit [35]. The working electrode was modified with polydopamine and reduced graphene oxide-MnO_2 nanoparticles to ensure the electrochemical oxidation of tryptophan at + 0.7 V using DPV. The *in vitro* investigations of the sensor within the pH range of 4.0–7.0 showed a linear detection range of tryptophan from 1 to 300 μM, and detection limits ranged between 0.22 and 0.39 μM. Moreover, the sensor exhibited an excellent anti-interfering ability towards different circulating molecules (indole-3-acetic acid, abscisic acid, salicylic acid, glucose, L-alanine, L-serine, maltose, and sucrose). Regarding the *in vivo* detection of tryptophan level in tomato fruit, the oxidation signal was observed from the 18th voltammogram, and the peak current was significantly reduced by the 32nd measurement, which can be assigned to the desorption of tryptophan from the electrode. Herein, the use of a glassy carbon electrode allowed for high electrocatalytic activity and selectivity towards the oxidation of tryptophan, but the large size of the developed sensor (WE:

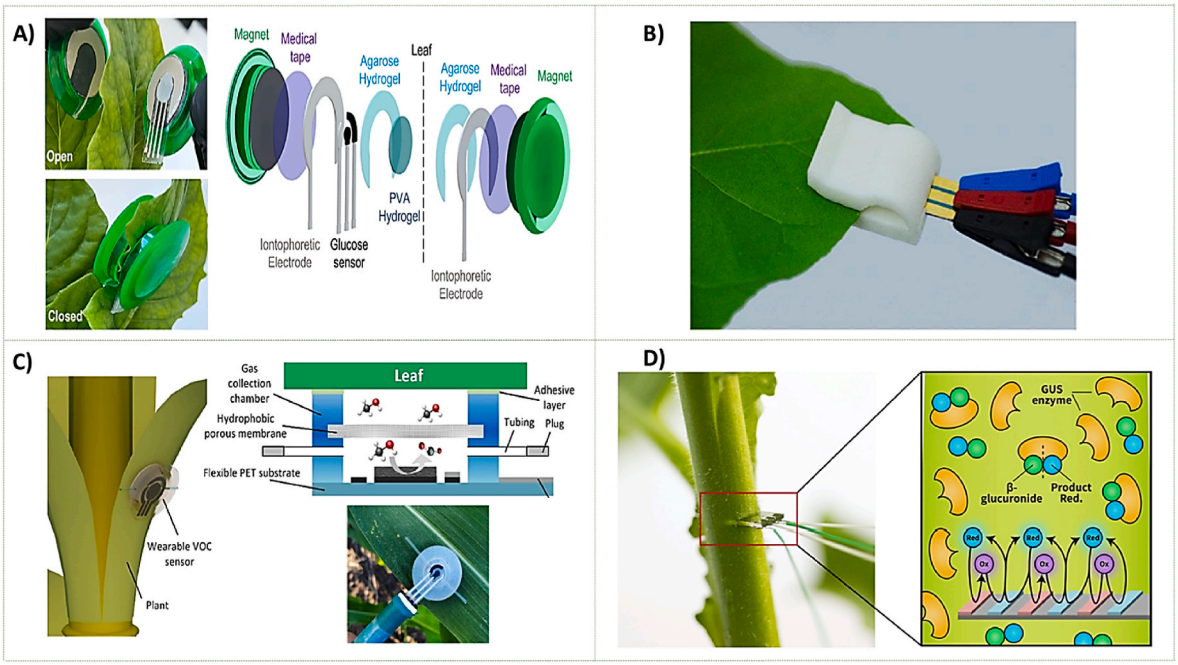


Fig. 5. A) A wearable electrochemical biosensor for glucose monitoring in leaves constructed on a poly(ethylene terephthalate) substrate and integrating a reverse iontophoresis glucose extraction system. Reprinted with permission from Ref. [38], B) A 3D printed holder clamping a three-electrode microchip to the abaxial side of the leaf for *in vivo* monitoring of β-glucuronidase activity under stress. Reprinted with permission from Ref. [39], C) A wearable volatile organic compounds sensor prepared on poly(ethylene terephthalate) and modified with poly(2-amino-1,3,4-thiadiazole) and platinum nanoparticles composite for the detection of methanol emission under abiotic stress. Reprinted with permission from Ref. [40], D) An implantable electrochemical planar chip inserted into the plant stem for monitoring the expression of β-glucuronidase under stress. Reprinted with permission from Ref. [42].

length × width × thickness: 10 × 20 × 1 mm) causes plant tissue damage upon electrode insertion, making the proposed sensor not suitable for the *in vivo* monitoring of tryptophan in small plants and small tissues.

Because of the large dimension of GCE, which may inevitably damage the plants and hinder their growth, a miniaturised sensing system based on a graphite rod electrode (GRE) modified with MWCNTs and poly(sulfosalicylic acid) film was developed [36]. By conducting *in vitro* analysis, the sensor exhibited a linear range of 10–110 μM and detection limits as low as 0.037–0.121 μM, as a function of the pH (4.0–4.8) of tryptophan solutions. As shown in Fig. 4A, the GRE (Φ = 2 mm) was inserted inside the tomato fruit together with the entire electrochemical system to allow the oxidation of tryptophan at around + 0.75 V using DPV, after an enrichment phase. The concentration of tryptophan was monitored in green, yellow, orange, and red tomato fruits, showing that the oxidation signal required 15 scans to become stable. Once again, the concentration of tryptophan in tomato fruit was found to be significantly dependent on the growth stage of cherry tomato fruits, ranging from 4.40 μM to 23.25 μM. Nonetheless, a considerable difference was observed in the tryptophan content of tomato fruit when compared with that measured in tomato juice. This can be ascribed to the inherent resistance of tomato fruit to the sensor insertion, which is capable of detecting tryptophan exclusively in direct contact with the tomato surface. Besides, abscisic acid phytohormone, which is an inhibitor of plant growth, was found to interfere with the detection of tryptophan using the developed sensor.

GRE (Φ = 2 mm) was also employed for constructing an implantable biosensor aiming at the detection of glutamate in cucumber fruit [37]. The GRE was modified with platinum nanoparticles and poly(*m*-phenylenediamine) film to improve the electron transfer on the surface of the electrode and exclude anion interference, respectively. To guarantee a selective detection of glutamate among other interfering molecules, a glutamate oxidase enzyme was used to oxidise glutamate, generating hydrogen peroxide (H_2O_2). The biosensor displayed good selectivity and excellent stability with a linear range of 2–550 μM and a limit of detection equal to 0.536 μM. For practical use, the enzymatic biosensor was inserted into the cucumber fruit, as illustrated in Fig. 4B. The study was made by injecting different concentrations of glutamate ranging from 0.1 to 5 μM into the fruit before conducting the amperometric measurements at + 0.4 V. The injection resulted in an enhancement of the current signal, indicating that the developed biosensor could be useful for studying plant growth.

2.4. Stress biomarkers

2.4.1. Wearable (bio)sensors

Glucose is a primary plant metabolite and a critical molecular modulator of various cellular processes ranging from germination to senescence. Monitoring this molecule in plants helps to understand the real-time metabolic response to stresses. In this regard, a wearable-like technology integrating a reverse iontophoresis (RI) glucose extraction system and an enzymatic glucose biosensor was developed for *in vivo* monitoring of glucose in plant leaves [38]. The biosensor comprises a magnetic cathode holding an iontophoretic electrode and a glucose oxidase-based biosensor printed on a poly(ethylene terephthalate) substrate. The cathode was equipped with a polyvinyl alcohol hydrogel acting as a reservoir and transport scaffold for moving the extracted glucose to the biosensor surface. Whereas, the anode magnetic section contains the positive terminal for the iontophoretic application. To protect plant leaves from physical damage, agarose hydrogel was used on both sides of the iontophoretic system, as depicted in Fig. 5A. By utilising two magnet parts and medical tape, the extraction and biosensing system can be sandwiched onto the plant leaf. Glucose flowed from the leaf towards the biosensor surface by performing chronopotentiometric measurements for 10 min with 0.2 mA/cm^2 current density. Before validating the potential applicability of the system in plants, its analytical performance was assessed using different glucose concentrations (20–80 μM) at pH 7.4, resulting in limits of detection and quantification equal to 9.4 μM and 28.5 μM, respectively, and improved enzymatic reaction rate at 40 °C. Although the assay involves three steps - pre-RI current measurement with chronoamperometric scans, application of RI, and post-RI current measurement - the developed set-up was successfully used to investigate the impact of light wavelengths (fluorescent, blue, red) and temperature (10 °C–40 °C) stresses on the photosynthetic rate of various plants, including sweet pepper, romaine lettuce, and gerbera. It is worth noting that using a magnet sandwich-type configuration facilitated the use and removal of the integrated set-up from the leaves without causing any damage. Furthermore, the biosensor's surface is protected from environmental changes, thereby rendering it suitable for long-term monitoring of glucose in plants.

The expression of certain enzymes can provide information about stress conditions. For example, the β-glucuronidase enzyme is a versatile reporter of gene expression that is up-regulated by stress and senescence in plants. To evaluate β-glucuronidase expression in tobacco leaves, its capacity to catalyse *p*-nitrophenol substrate into an electroactive by-product was investigated [39]. The *in vivo* sensing consists of clamping a three-electrode microchip made of gold to the plant leaf with the help of polydimethylsiloxane, as shown in Fig. 5B. The expression of β-glucuronidase under stress (40 °C for 2 h) induces the catalysis of the substrate added to the leaf, generating phosphate that traverses out of the plant cell and gets oxidised on the working electrode using chronoamperometric measurements. First, by performing *in vitro* experiments with MSK8 plant cells, expressing the β-glucuronidase enzyme, in solution with the enzymatic substrate, a detection limit equal to 0.1 mM was achieved. The *in vivo* study of the impact of heat shock on the expression of β-glucuronidase enzyme in the *Nicotiana tabacum* plant revealed a notable increase in the current signal, which corresponded to the elevated expression of the enzyme under heat stress conditions.

Stress levels in plants can be monitored by observing the volatile organic compounds they emit (e.g., methanol) as a defence mechanism against microbial invasion. In this regard, a three-electrode system was prepared on poly(ethylene terephthalate), then the working electrode was modified with a composite of conducting poly(2-amino-1,3,4-thiadiazole) and platinum nanoparticles that together enable efficient electrochemical oxidation of methanol at + 0.47 V [40]. To ensure the collection of gaseous methanol emitted by the leaf, the sensing platform was integrated into a miniature gas collection chamber capped with a hydrophobic gas diffusion membrane, thus minimising the influence of moisture on the sensor performance, as depicted in Fig. 5C. The sensor showed a difference in methanol emission between the lower (9.4 ± 4.8 ppm) and upper (22.6 ± 5.7 ppm) leaves of greenhouse maize plants. Under field conditions, the sensor revealed a noticeable difference in methanol emission concentration, ranging from 34.5 ± 24.8 to 51.4 ± 27.2 ppm, between two genotypes (Mo17 and B73 inbred lines) of maize plants, confirming that the developed sensor can serve as a smart device for monitoring methanol in the gaseous phase. The detection of volatile compounds over a multitude of molecules found in plants in different states (liquid or gaseous) offers more advantageous applications, as no extraction system of these molecules is needed, unlike gas chromatography-mass spectrometry, which requires laboratory set-up processes and skilled operators.

2.4.2. Implantable (bio)sensors

Monitoring glucose in plants was also achieved using a hollow microneedle biosensor with an aperture diameter of 300 μm, which minimises damage to the plants while penetrating the cuticle barrier [41]. The electrochemical system, which constitutes the internal component of the microneedle biosensor, consists of reference and counter microelectrode wires, and a platinum wire working electrode modified with gold nanoparticles, Nafion, glucose oxidase, and polyurethane. The device was thus constructed by encapsulating the

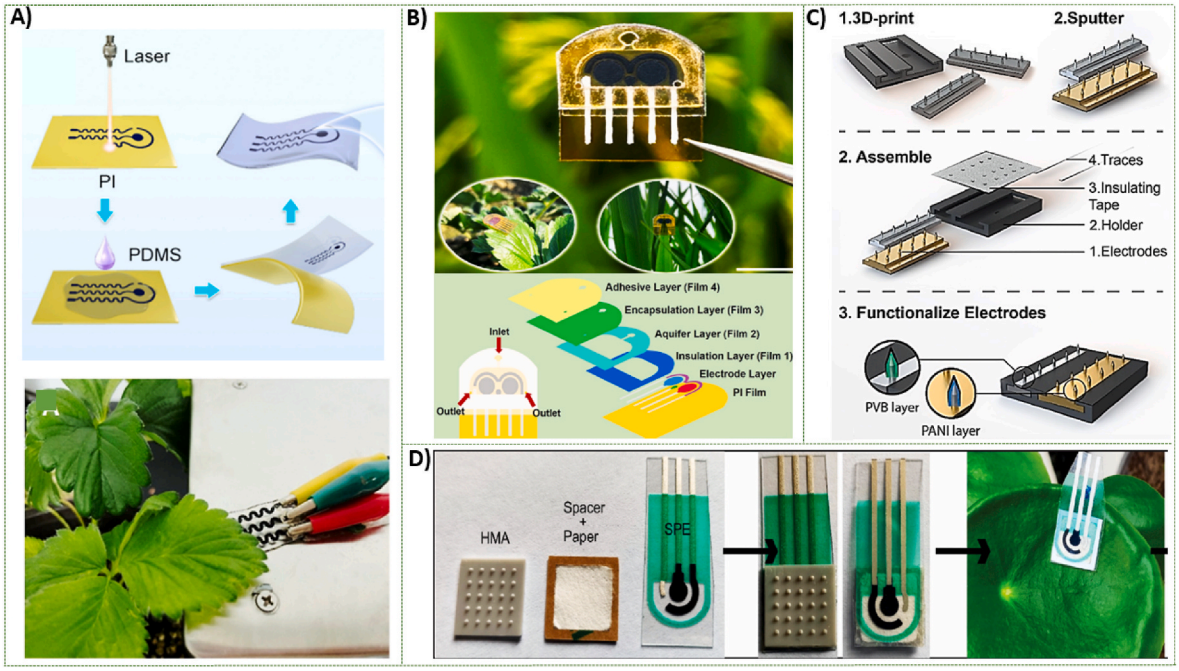


Fig. 6. A) A wearable and flexible laser-induced graphene sensor for gallic acid detection in strawberry leaves. Reprinted with permission from Ref. [44], B) A wearable electrochemical sensor for multiplexed monitoring of pH, salicylic acid, and neonicotinoid insecticide in plant guttation. Reprinted with permission from Ref. [47], C) A 3D-microneedle-based electrochemical sensor for pH monitoring in leaf sap. Reprinted with permission from Ref. [48], D) Screen-printed electrodes-based (bio)sensor coupled with a 3D printed hollow microneedle extracting patch for plant molecules analysis. Reprinted with permission from Ref. [49].

microelectrodes inside the microneedle mold, which was obtained by 3D printing technology.

The capability of the microneedle biosensor to detect glucose was first evaluated *in vitro*, using chronoamperometry at + 0.7 V, resulting in a detection range of 100 μM to 100 mM, a limit of detection of 33.3 μM, and a good anti-interference performance in the presence of different circulating molecules. Furthermore, an analysis of the grinding solution of three well-grown tomato stems fortified with 100 μM and 5 mM of glucose demonstrated recovery rates of 92 %–118 %, thereby confirming that the complexity of the plant matrix may not impede the analysis of glucose.

To conduct *in vivo* glucose monitoring, the microneedle biosensor was inserted into the stems of tomato plants and the leaves of Aloe vera plants for 12 h. The results obtained indicated that the current signals exhibited by the microneedle biosensor were conditional on the photosynthetic state, which exhibited a nocturnal and diurnal variation. Indeed, low current signals were recorded during nocturnal periods, concomitant with glucose consumption. Conversely, high current signals were observed diurnally, as a consequence of glucose synthesis and subsequent accumulation. Furthermore, a low current signal was observed with tomatoes grown under salt stress, which is explicable by the inhibition of photosynthesis in the presence of high concentrations of salt.

In this study, the microneedle biosensor demonstrates significant potential for real-time glucose sensing. However, the primary challenges are the presence of glucose at varying concentrations in the plant parts and its potential migration from the insertion site due to the movement of the xylem and phloem throughout the stem.

Implantable sensors have also been developed to estimate the expression of β-glucuronidase under stress on the plant stem [42]. A planar chip was fabricated on a glass substrate to enable perpendicular insertion into the plant stem, as shown in Fig. 5D. The expression of β-glucuronidase was monitored after the addition of 4-nitrophenyl-D-glucopyranoside substrate into the cross-section of the stem, releasing *p*-nitrophenol that was monitored after 10 min using cyclic voltammetry. Stem-implantable biosensors are mechanically more stable and less sensitive to environmental changes than leaf-mounted biosensors reported in previous works. However, a decrease in the signal was observed within a few minutes. This may be due to the stem not being a closed system, allowing the enzymatic product to be easily transported away from the working electrode due to the movement of the xylem and phloem throughout the stem.

2.5. Reactive oxygen species (ROS) and related compounds

2.5.1. Wearable (bio)sensors

In addition to the phytohormones previously discussed, reactive oxygen species (ROS) represent a class of signaling molecules that are generated during the initial stages of the plant stress response. These ROS can traverse plant cells during signal transduction, inducing a transition from a normal growth state to a stress state in various cells and tissues. However, excessive ROS lead to oxidative burst and biomolecules damage. The resulting damage negatively affects plant growth, development, and ultimately survival [43].

Gallic acid (GA) is a prominent polyphenolic organic compound present in plants. It possesses strong antioxidant properties, which aid in the scavenging of excess ROS and, consequently, the mitigation of oxidative stress in plants. To ascertain the presence of GA in strawberry leaves, a wearable sensor composed of flexible LIG-based serpentine electrodes was adhered to the leaves [44]. The oxidation of GA was performed on MXene/molybdenum disulfide-modified electrodes, on which the synergetic effect of both compounds, in addition to graphene, improved the conductivity and the electrocatalytic ability of the sensor. The oxidation peak of GA was monitored at + 0.35 V under a pH of 3, and the DPV responses demonstrated a limit of detection of 0.625 μM within the analytical range of 1–1000 μM. The developed sensor exhibited selectivity towards 13 interfering molecules, a high reproducibility (RSD = 4.43 %), and an acceptable storage stability for 14 days. The serpentine sensor demonstrated optimal tensile properties, thus facilitating its adhesion to the lower surface of strawberry leaves, as shown in Fig. 6A, for *in vivo* monitoring of GA under salt stress. The creation of a small aperture on the leaf enabled the flow of GA towards

the surface of the electrode, accompanied by 20 μL of PBS (pH 3). The findings indicate that under 0 mM and 100 mM NaCl salt stress, the GA contents in strawberry leaves were 12.99 ± 4.76 and 38.65 ± 15.96 μM, respectively, which confirms that under salt stress, plants enhance the synthesis of phenolic compounds to attenuate the oxidative stress effects. However, adding a buffer solution to the punching hole before analysis resulted in diluting the analyte, consequently leading to an underestimation of the real GA content.

Glycine betaine (GB) is a bioactive molecule found in a wide range of plant species. Its biosynthesis is often triggered by abiotic stress (e.g., salt, drought, and low temperature), and it plays a crucial role in inhibiting the accumulation of ROS. The *in vivo* determination of GB in plants was performed using a MIP biosensor, which was constructed on screen-printed electrodes (SPEs) [45]. The fabrication of the MIP biosensor was conducted in a series of steps: (i) the electrodeposition of gold nanoparticles (AuNPs) on SPEs to enhance the conductivity of the biosensor, (ii) the electropolymerisation of thionine (Thi), the reference signal molecule, on AuNPs-SPEs, and iii) the modification of pThi/AuNPs/SPEs with MIP, which was prepared by the polymerisation of dopamine under alkaline conditions on MWCNTs in the presence of GB. The sensing principle of the developed biosensor is based on monitoring the oxidation peak of pThi at – 0.3 V using DPV. The current response of pThi exhibited a gradual downward trend as the GB concentration increased, which is attributed to the occupation of the imprinted cavities by the GB molecules. The biosensor demonstrated a detection limit of 0.707 fM when incubated with GB solutions for 10 min, within the analytical range of 1 fM-10 mM. Additionally, the biosensor showed excellent selectivity among eight interfering molecules, good repeatability (RSD = 8 %), and high stability during 14 days.

For the *in vivo* detection, small holes were made on the leaf surface of cucumber fruit, and the biosensor was firmly attached to the hole using adhesive tape. The addition of phosphate buffer solution (20 μL) to the hole resulted in the flow of GB present in the leaves towards the working electrode. The results obtained demonstrated that the concentration of GB found in cucumber leaves grown under salt stress was equal to (6.61 ± 0.83) μM, in comparison with (2.43 ± 0.36) μM in the absence of salt.

Once again, the addition of PBS onto the leaves to meet the requirements of electrochemical testing resulted in a dilution of the analyte, and thus an underestimation of hundreds of times the real content of GB, compared to the HPLC reference method. On the other hand, the standard addition method was employed in the recovery tests to ascertain the practical usefulness of the biosensor for cucumber leaves. The recoveries obtained by adding a GB standard solution to cucumber juice were very encouraging (96.97 %–107.09 %). However, it should be noted that the juice used for the recovery study was obtained from ground cucumber fruit samples and not from cucumber leaves, which undoubtedly present a different composition compared to cucumber fruit. Furthermore, the use of conventional SPE restricts the applicability of the developed biosensor to plants with planar surfaces, excluding stems and fruits, which may present an interesting amount of GB compared to leaves, and thus provide more reliable results.

2.5.2. Implantable sensors

Among the various ROS, H_2O_2 is a particularly prominent mediator of rapid systemic signals in plants, owing to its prolonged half-life and capacity for long-distance and transmembrane transmission. In this regard, a novel implantable microsensor was developed for the continuous monitoring of H_2O_2 in tomato stems [46]. The microsensor comprises three porous LIG microelectrodes, modified with electrocatalytic platinum nanoparticles and Nafion to ensure the electrochemical oxidation of H_2O_2 at + 0.6 V using chronoamperometry. To ensure the self-powered operation of the sensing device, a photovoltaic module combined with a data acquisition and transmission module was employed. This module was capable of collecting light in the planting environment and powering the microsensor continuously. Under optimal detection conditions, the microsensor demonstrated a detection limit of 0.35 μM within the linear range of 2–200 μM. Furthermore, the incorporation of Nafion film on the working and reference electrodes resulted in enhanced selectivity of the microsensor in the presence of various interferents (e.g., ascorbic acid), while maintaining stability across a broad pH range (from 5 to 8). The self-powered sensing system was used to monitor the dynamic H_2O_2 levels in tomato plants in real time under osmotic, UV, and mechanical injury abiotic stress. A 2 mm incision was made on the tomato stem to insert the microsensor, after which it was found that the H_2O_2 concentration generated under various stresses ranged from 10 to 100 μM. However, the H_2O_2 signal induced by osmotic stress lasted for 10 h, in contrast to 10 min and 10 s in the case of UV and mechanical stress, respectively. This suggests that tomato plants possess the capacity to effectively cope with certain mechanical stresses during routine growth. However, under conditions of extreme osmotic stress and UV radiation, tomato plants produce high concentrations of H_2O_2 to counteract the stress-induced damage. In this study, the developed microsensor demonstrated its capacity to monitor H_2O_2 level in tomato stems under abiotic stress. However, the presence of peroxidase in the phloem and xylem sap of the plant had a significant impact on the results. Furthermore, the sensor demonstrated enhanced analytical performance at elevated temperatures and was sensitive to external factors, including wind, contact, and the way of inserting the microsensor into the stem.

2.6. pH

2.6.1. Wearable sensors

The monitoring the pH level in plants is a critical aspect of plant biology. This is because it facilitates comprehension of the plant's physiological state and identification of any potential health concerns. Alterations in the internal pH of a plant have substantial repercussions on various physiological processes, including growth, nutrient uptake, enzyme activity, stress resistance, and the quality of final metabolites.

In this regard, a noninvasive wearable electrochemical sensor has been developed for monitoring the pH level together with salicylic acid, and neonicotinoid insecticide in plant leaves by analysing plant guttation droplets [47]. The sensor electrodes were prepared using a LIG printing method, holding counter and reference electrodes, in addition to three working electrodes; two unmodified electrodes for the detection of salicylic acid and neonicotinoid insecticide, while the third working electrode was modified with a polyaniline layer to monitor pH variation. To ensure sufficient guttation volume for the electrochemical analysis, a guttation fluid collection module was prepared and positioned on the plant leaf. As illustrated in Fig. 6B, the assembly of layers of polyethylene terephthalate films was undertaken to form the liquid storage layer (film 2), the sealing film for the guttation fluid layer (film 3), and the connection between the guttation fluid layer and the plant leaves (film 4). The total liquid storage chamber was able to collect 26.4 μL of guttation liquid.

The monitoring of salicylic acid at + 0.5 V and neonicotinoid insecticide at - 1.15 V using SWV revealed a satisfactory linear relationship between the analyte concentration and the peak signal within the analytical ranges of 0–13.8 mg L^{-1} and 0–50 mg L^{-1} for salicylic acid and neonicotinoid insecticide, respectively. In addition, high selectivity for both analytes was observed in the presence of several interfering molecules. The study of the reproducibility and repeatability of the sensor showed values of RSD below 5.1 % and 11.6 % for salicylic acid and neonicotinoid insecticide, respectively. The chronopotentiometric test of the pH sensor within a pH range of 4.5–8.5 gave good results with a sensitivity of 47 mV.pH^{-1}, in addition to good stability during 50 s.

The sensor was attached to the leaves of rice plants cultivated under salt stress conditions, and the analysis of the guttation fluid revealed that the concentration of the insecticide increased during the initial days of exposure, subsequently decreasing. This phenomenon can be ascribed to the plant's capacity to eliminate the insecticide. A similar trend was observed for salicylic acid, indicating that the plant possesses the ability

to withstand salt stress, thereby ceasing the synthesis of salicylic acid. However, the pH profiling of the plant exhibited random fluctuations, even if the plant was grown under controlled conditions, indicating that the developed sensor still requires significant improvements to fully comprehend the plant's physiological responses.

2.6.2. Implantable sensors

Apart from wearable sensors, a 3D printed solid microneedle potentiometric sensor was constructed for the continuous monitoring of pH fluctuations in plants under abiotic stress [48]. As demonstrated in Fig. 6C, two microneedle arrays were printed using stereolithography technology, and then sputtered with gold and silver to form the working and the reference electrodes, respectively. To ensure the sensor's sensitivity to pH variation, polyaniline was electrodeposited on the working electrode. Meanwhile, a polyvinyl butyral membrane was deposited by drop casting on the reference electrode, thereby ensuring potential stability regardless of the composition of plant sap. Upon assembly of the system into two microneedle electrodes, a planar screen-printed connector was integrated for an easy plug-in to the potentiostat.

The electrochemical evaluation of the developed sensor in Britton-Robinson buffer solutions (pH 4 to pH 8) demonstrated a time of response of less than 50 s to obtain 90 % of the response, excellent linearity (near-Nernstian response of - 57.2 mV pH^{-1}), excellent selectivity (near-Nernstian response of −61.5 mV pH^{-1}), high reversibility (near-Nernstian response of −58.4 mV pH^{-1}), and slight influence of temperature. Furthermore, the sensor was tested in the plant sap extracted from the leaves, showing overlapping calibration curves before and after sap analysis. This indicates that the composition of the sap matrix does not influence pH monitoring.

The *in vivo* applicability of the developed sensor was investigated on plant sap leaves under drought and watering conditions. The microneedle sensors were firmly attached to the leaves using tape or a magnet. By piercing two sensors (1 and 2) of different leaves of the same plant, an average variation of 0.085 ± 0.079 pH units between the two sensors was observed, demonstrating the high reproducibility of the microneedle sensors. Moreover, the pH level at the initiation of the *in vivo* test was recorded at 5.61 and 5.68 for sensors 1 and 2, respectively, which is comparable to the pH level analysed *ex vivo* (extracted plant sap) using the same sensors (pH 5.71 and 5.47, respectively).

Furthermore, the microneedle sensor demonstrated the capacity to register pH variations in response to prevailing environmental conditions (i.e. drought and watering) and exhibited a tendency to display less acidic pH values under conditions of drought stress (pH 6.93 ± 0.34) in comparison to the initial hour of drought stress (pH 5.34 ± 0.28). Watering the plant resulted in a decline in pH value (pH 6.12 ± 0.23), indicating a modest recovery of the normal pH status. Similar observations were recorded when the sensors were attached to another plant species, thus confirming the usefulness of the sensor developed for *in vivo* monitoring of pH variations. Nevertheless, further efforts are required to address the potential drift observed during the experiments, as this is the most common problem encountered with potentiometric sensors.

The same group has developed a low-cost 3D-printed hollow microneedle patch coupled with polyester screen-printed electrochemical (bio)sensors for the determination of pH, H_2O_2, and glucose in plants using individual sensors [49]. As demonstrated in Fig. 6D, the microneedle patch functions as a sampling device, facilitating the extraction of plant fluid through thumb pressing and subsequent flow towards a filter paper collecting pad, before reaching the surface of the sensor. The detection of diverse plant analytes was achieved through the modification of separate sensors by the electrodeposition of polyaniline, Prussian blue, or Prussian blue in conjunction with glucose oxidase, for monitoring the pH, H_2O_2, and glucose, respectively. The analytical characterisation of each sensor was previously performed by the same group.

The *in vivo* assessment of the (bio)sensors was conducted by piercing the leaves of different plant species (Plant 1 - *Pilea peperomioides*; Plant 2 - *Curio rowleyanus*; Plant 3 - *Zamioculcas zamiifolia*; Plant 4 - *Echeveria Raindrops*) using the microneedle patch. Each analyte was monitored in the leaf fluid, extracted using standard methodology, or by the developed microneedle patch. The pH of the apoplast fluid of the four plants was measured, with levels ranging from 5.2 to 6.1. The highest and lowest levels of acidity were exhibited by Plants 4 and 3, respectively (i.e. pH 5.2 ± 0.1 and pH 6.1 ± 0.2). On the other hand, the chronoamperograms of H_2O_2 indicated that plant 1 exhibited a significant discrepancy (40.5 ± 1.7 %) between the two extraction methods, potentially attributable to a delay in analysing the samples. In contrast, the levels of H_2O_2 in the leaf of plant 4 remained relatively consistent (12.5 ± 0.9 % of difference) across both methods. The analysis of glucose revealed a variation of 3.6 ± 3.2 % and 5.7 ± 5.6 % between the two extraction methods during the analysis of plant 1 and plant 4, respectively.

The present study raises several research questions that require further consideration. Firstly, it is necessary to ascertain the suitability of the microneedle configuration for the extraction of plant circulating molecules, as different levels were obtained for H_2O_2, for example. Secondly, it is important to determine whether the microneedle configuration can be used for the extraction of other analytes. Thirdly, it is essential to take into account the differences in the abundance of analytes from leaves to stems and other parts of the plant. Finally, the study also poses a question regarding the suitability of the entire system (microneedles coupled with polyester screen-printed electrodes) for use on irregular and curvy plant surfaces.

3. Discussion and conclusions

Great interest has recently grown in using wearable and implantable (bio)sensors to understand changes in the plant's environment, such as the excessive use of agrochemicals and stress conditions.

Wearable (bio)sensors are designed to be worn directly on plant surfaces, such as fruits, leaves, and stems. They are typically flexible and stretchable, and their construction requires using materials with excellent tenacity and chemical resistance. Plant wearable (bio)sensors are currently constructed using flexible materials, such as cellulose (e.g., cellulose acetate, parchment paper, and office paper), wood pulp (i.e., kraft paper), carbon materials (e.g., carbon tape and laser-induced graphene), and thermoplastic polymers (e.g., polyethylene terephthalate and poly(lactic acid)). These materials enable the (bio)sensors to bend like flexible skin, conforming to organisms with a radius of curvature of less than 100 μm. Furthermore, wearable (bio)sensors can be attached to the surface of plants and modified with various nanomaterials, including gold nanoparticles, platinum nanoparticles, carbon black, multi-walled carbon nanotubes, and Prussian blue, to enhance the sensor's electrochemical performance without affecting the plant's function.

However, the use of flexible (bio)sensors made from inexpensive substrates may not provide an accurate reflection of the concentration of a specific molecule within the plant system. For instance, pre-made electrodes may not conform to irregular surfaces, which can impair the accuracy of the collected data. Moreover, the analyte to be detected is often applied to the sensor surface before analysis, or diluted by adding a buffer solution to meet the requirements of electrochemical testing, which in turn affect accuracy. Wearable (bio)sensors made from lightweight materials may not be suitable for use in changing environmental conditions, such as wind and rain, unless the sensor is firmly attached to the plant surface. On the other hand, wearable sensors may be more effective than traditional methods in monitoring volatile molecules, such as methanol, as they do not require an extraction system. The efficacy of flexible sensors in monitoring volatile compounds has also been evidenced within the medical field through the development of pressure sensors capable of monitoring pressure changes in real-time

Table 1
Classification of different electrochemical (bio)sensors devoted to monitoring different key analytes in plants.

Analyte	Category	Sensing platform	Sensing principle	Electrochemical method	Plant part	(Bio)sensor type	Ref
Carbendazim	Pesticides	Kraft paper-based SPE (acidic and neutral treatment)	Direct oxidation	Differential pulse voltammetry	Apple and cabbage	Wearable	[22]
Carbendazim		Poly(lactic acid)-based SPE (acidic treatment)	Direct oxidation	Differential pulse voltammetry	Apple and cabbage skins	Wearable	[23]
Diquat			Direct oxidation	Square wave voltammetry			
Carbendazim		Cellulose acetate-based SPE	Direct oxidation	Differential pulse voltammetry	Lettuce and tomato fruit	Wearable	[24]
Paraquat			Direct oxidation	Square wave voltammetry			
Methyl parathion		LIG electrode/AuNPs/Nafion/OPH	Enzymatic reaction	Square wave voltammetry	Spinach leaves and apple fruit	Wearable	[25]
		LIG-based gold electrode/Lipase	Enzymatic reaction	Differential pulse voltammetry	*Epipremnum aureum* and lettuce leaves	Wearable	[26]
Paraoxon		Office paper-based SPE/CB/PBNPs and filter paper/BChE	Enzymatic reaction	Chronoamperometry	Grass	Wearable	[27]
2,4-dichlorophenoxyacetic acid		Office paper-based SPE/CB and filter paper/ALP	Enzymatic reaction				
Glyphosate		Office paper-based SPE/CB and filter paper/HRP	Enzymatic reaction				
Neonicotinoid		LIG electrode	Direct oxidation	Square wave voltammetry	Rice leaves	Wearable	[47]
Salicylic acid	Phytohormone	Carbon paper-based electrodes/MWCNTs/Nafion	Direct oxidation	Differential pulse voltammetry	Tomato leaves	Wearable	[28]
		LIG electrode coupled with a reverse iontophoretic extraction system	Direct oxidation	Chronoamperometry	Avocado plant leaves	Wearable	[29]
		Interdigitated electrodes/Au@Cu_2O/graphene/PDA	Direct oxidation	Amperometry	Cucumber leaves	Wearable	[30]
		Interdigitated electrodes/Microneedles/magnetic MIP	Direct oxidation	Chronoamperometry	Tobacco leaves	Wearable	[31]
		LIG electrode	Direct reduction	Square wave voltammetry	Rice leaves	Wearable	[47]
Abscisic acid		Ta microelectrodes/VG/Au@SnO_2	Direct oxidation	Amperometry	Cucumber fruit	Implantable	[32]
Indole-3-acetic acid		Anodised SS electrode/Au/PtNPs/rGO/PST	Direct oxidation	Differential pulse voltammetry	Soybean stem	Implantable	[33]
		Vertical/horizontal graphene microneedle electrode	Direct oxidation	Differential pulse voltammetry	Cucumber and cauliflower	Implantable	[34]
Tryptophan	Growth precursors	GCE/PDA/rGO/MnO_2	Direct oxidation	Differential pulse voltammetry	Tomato fruit	Implantable	[35]
		GRE/MWCNTs/PSA	Direct oxidation	Differential pulse voltammetry	Tomato fruit	Implantable	[36]
Glutamate		GRE/PtNPs/PMPD/GluOx	Enzymatic reaction	Amperometry	Cucumber fruit	Implantable	[37]
Glucose	Stress biomarker	PET-based electrodes/Prussian blue carbon ink/GOx	Enzymatic reaction	Amperometry	Leaves (sweet pepper, gerbera, and romaine lettuce)	Wearable	[38]
		Microneedle/Pt electrode/AuNPs/Nafion/GOx/PU	Enzymatic reaction	Chronoamperometry	Tomato stem and Aloe vera leaf	Implantable	[41]
		SPE/PB/GOx/BSA/Chitosan	Enzymatic reaction	Chronoamperometry	Plant leaves	Implantable	[49]
β-glucuronidase		Gold chip	Enzymatic reaction	Chronoamperometry	Tobacco leaves	Wearable	[39]
		Interdigitated-electrode arrays made of gold	Enzymatic reaction	Cyclic voltammetry	Tobacco stem	Implantable	[42]
Methanol		PET-based electrode/poly(ATD)/PtNPs	Direct oxidation	Chronoamperometry	Maize leaves	Wearable	[40]
Hydrogen peroxide	Reactive oxygen species	LIG/PtNPs/Nafion	Direct oxidation	Chronoamperometry	Tomato stems	Implantable	[46]
		SPE/PB	Direct reduction	Chronoamperometry	Plant leaves	Implantable	[49]
Gallic acid		LIG/MXene/MoS_2	Direct oxidation	Differential pulse voltammetry	Strawberry leaves	Wearable	[44]
Glycine betaine		SPE/AuNPs/pThi/MIP-MWCNTs	pThi oxidation	Differential pulse voltammetry	Cucumber leaf	Wearable	[45]
pH	Indicator of physiological activity	LIG/PANI	Near-Nernstian response	Potentiometry	Rice leaves	Wearable	[47]
		Microneedle/AuNPs/PANI	Near-Nernstian response	Potentiometry	Plant leaves	Implantable	[48]

(*continued on next page*)

Table 1 (*continued*)

Analyte	Category	Sensing platform	Sensing principle	Electrochemical method	Plant part	(Bio)sensor type	Ref
		SPE/PANI	Near-Nernstian response	Potentiometry	Plant leaves	Implantable	[49]

AuNPs: Gold nanoparticles; OPH: Organophosphorus hydrolase; CB: Carbon black; PBNPs: Prussian blue nanoparticles; BChE: Butyrylcholinesterase; ALP: Alkaline phosphatase; HRP: Horseradish peroxidase; BSA: Bovine serum albumine; MWCNTs: Multiwalled carbon nanotubes; MIP: Molecularly imprinted polymer; Ta: Tantalum; VG: Vertical graphene; Au@SnO_2: Gold–Tin (IV) oxide Core-shell nanoparticles; SS electrode: Stainless steel electrode; PtNPs: Platinum nanoparticles; rGO: Reduced graphene oxide; PST: Poly(safranine T); PET: Polyethylene terephthalate; GOx: Glucose oxidase; PU: Polyurethane; Poly(ATD): poly(2-amino-1,3,4-thiadiazole); MoS_2: Molybdenum disulfide; pThi: Polythionine; LIG: Laser-induced graphene; PANI: Polyaniline; GCE: Glassy carbon electrode; SPE: Screen-printed electrodes; PDA: polydopamine; MnO_2: Manganese dioxide; GRE: Graphite rod electrode; PSA: poly (sulfosalicylic acid) film; PMPD: poly (*m*-phenylenediamine) film; GluOx: Glutamate oxidase.

[50–53]. Plant wearable (bio)sensors can also be useful for real-time monitoring of excessive use of agrochemicals on crops by quantifying the concentration of pesticides in the aerosol phase.

An alternative technology for monitoring circulating molecules in plants is through implantable electrochemical sensors that can be directly inserted into the plant. These (bio)sensors are typically made from materials known for their corrosion resistance and excellent conductivity, such as tantalum wires, stainless steel wires, gold chips, glassy carbon material, and graphite rod electrodes. Rigid materials of varying thicknesses, ranging from 0.2 to 2 mm, can be used to form a three-electrode system that can be inserted into the plant system without causing significant damage. Using rigid (bio)sensors that can be inserted inside the plant offers the advantage of monitoring a target molecule with greater accuracy. The target analyte can be detected directly inside the plant system after an accumulation period, without the need to add or spray the analyte onto the plant surface as required for flexible sensors. However, caution must be exercised when inserting the (bio)sensors to avoid hindering plant growth or inducing senescence. Besides, using implantable devices may not reflect the real content of a specific analyte, as the latter can be removed from the insertion zone by the movement of the xylem and phloem throughout the stem. In general, rigid (bio)sensors are more suitable for insertion into the stem of mature plants, as they cannot be inserted into leaves, slender stems, or fragile seedlings.

In addition to the (bio)sensors mentioned earlier, which are fabricated outside the plant, plant key analytes can also be monitored using a plant sensor written directly on crop surfaces. This has been reported for the detection of methyl parathion and nitrate [54]. However, writing sensors directly onto plant surfaces may be less convenient for decentralised applications as the ink needs to be prepared, applied to the plant, dried, and finally used.

Despite the scientific progress in the field of plant (bio)sensors, which has demonstrated considerable potential for applications, the implementation of electrochemical (bio)sensors for monitoring plant health remains underdeveloped and necessitates technological enhancements. A significant barrier to the expansion of the applications of plant (bio)sensors is the necessity for enhanced robustness and long-term monitoring stability. To date, most reported (bio)sensors have been evaluated in controlled environments, where (bio)sensors are firmly affixed to plant sections or directly implanted into stems for short monitoring periods. However, conducting in-field analysis, which is subject to variations in temperature, humidity, wind, and the presence of insects, will undoubtedly alter the analytical performance of non-robust (bio)sensors. Furthermore, it is imperative to consider the application of these (bio)sensors across diverse plant species, given their current limitation to repetitive plant samples (e.g., tomato, cucumber, and apple fruits). Concerning the fabrication of (bio)sensing platforms, attention to raw materials and nanomodifiers is relevant to mitigate the adverse effects of analytical platforms on plant growth. Furthermore, a trade-off between cost-effectiveness and high performance is indispensable to ensure the commercial applicability of these sensors.

Therefore, producing a performant (bio)sensor with promising applications in plant health monitoring is conditional upon fulfilling several requirements. Firstly, the (bio)sensor must be capable of fast analysis, as the target analyte can be rapidly removed by the plant's vascular system. Secondly, stable signal readout and reproducible data must be obtained for accurate analysis. Rigorous validation of the (bio) sensors on diverse plant species and plant parts is also necessary, given the non-uniform distribution of analyte content within plant parts. Table 1 summarises different electrochemical (bio)sensors reported for *in vivo* monitoring of plant molecules.

On the other hand, the integration of artificial intelligence (AI) with plant sensors can provide valuable additional insights. For example, AI can collect and analyse data from i) leaf sensors to detect early signs of stress (biotic and abiotic) and predict plant diseases; ii) light sensors to optimise lighting conditions and thus photosynthesis for indoor greenhouses; and iii) humidity sensors to detect favorable humidity levels to plant growth and thus adjusting the irrigation systems. Furthermore, the combination of plant (bio)sensors and AI-powered robotic systems holds considerable potential to enhance agricultural efficiency and productivity. These sensors enable robots to adapt to environmental conditions, facilitating tasks such as planting, weeding, and harvesting. This development paves the way for a novel paradigm in agri-food practices, offering a promising avenue for the future of farming.

In addition to the environmental applications of AI robots, the exploitation of AI in developing electrochemical (bio)sensors for agricultural purposes has the potential to boost this evolving field significantly. Primarily, AI tools can aid in rapidly selecting suitable sensing materials from a vast pool, depending on the plant status, environmental conditions, and the intended application. As previously discussed, this process can reduce the time required for research and facilitate the development of robust (bio)sensing devices, a key challenge in plant (bio)sensor utilisation. Moreover, AI and its associated algorithms can facilitate the effective collection and processing of enormous datasets. This is particularly relevant in monitoring plant health, which is influenced by many biological, chemical, and physical factors. The concurrent monitoring of these factors is of the utmost importance and necessitates the deployment of multiple sensors to gain a comprehensive understanding of a particular plant's condition. Furthermore, AI can serve in programming (bio)sensors, thereby ensuring their activation or deactivation as required. This capability is particularly advantageous in scenarios necessitating uninterrupted and prolonged monitoring, as it eliminates the need to replace sensors manually.

CRediT authorship contribution statement

Narjiss Seddaoui: Conceptualization, Writing – original draft, Writing – review & editing. **Fabiana Arduini:** Conceptualization, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

Acknowledgements

F. Arduini thanks Horizon Europe COP-PILOT project, grant agreement 101189819.

Data availability

No data was used for the research described in the article.

References

[1] H.C. Koydemir, A. Ozcan, Wearable and implantable sensors for biomedical applications, Annu. Rev. Anal. Chem. 11 (2018) 127–146, https://doi.org/10.1146/annurev-anchem.
[2] Z. Yu, D. Tang, Artificial neural network-assisted wearable flexible sweat patch for drug management in parkinson's patients based on vacancy-engineered processing of g-C3N4, Anal. Chem. 94 (2022) 18000–18008, https://doi.org/10.1021/acs.analchem.2c04291.
[3] J. Qin, Y. Tang, Y. Zeng, X. Liu, D. Tang, Recent advances in flexible sensors: from sensing materials to detection modes, TrAC, Trends Anal. Chem. 181 (2024) 118027, https://doi.org/10.1016/j.trac.2024.118027.
[4] P.G. Steeneken, E. Kaiser, G.J. Verbiest, M.C. ten Veldhuis, Sensors in agriculture: towards an internet of plants, Nature Reviews Methods Primers 3 (2023) 60, https://doi.org/10.1038/s43586-023-00250-x.
[5] Forum Agenda and Frontiers Media S.A., Top 10 emerging technologies of 2023. https://www.weforum.org/publications/top-10-emerging-technologies-of-2023/, 2023.
[6] Y. Fang, R.P. Ramasamy, Current and prospective methods for plant disease detection, Biosensors. 5 (2015) 537–561, https://doi.org/10.3390/bios5030537.
[7] J.P. Giraldo, H. Wu, G.M. Newkirk, S. Kruss, Nanobiotechnology approaches for engineering smart plant sensors, Nat. Nanotechnol. 14 (2019) 541–553, https://doi.org/10.1038/s41565-019-0470-6.
[8] H. Yin, Y. Cao, B. Marelli, X. Zeng, A.J. Mason, C. Cao, Soil sensors and plant wearables for smart and precision agriculture, Adv. Mater. 33 (2021) 2007764, https://doi.org/10.1002/adma.202007764.
[9] C.C. Qu, X.Y. Sun, W.X. Sun, L.X. Cao, X.Q. Wang, Z.Z. He, Flexible wearables for plants, Small. 17 (2021) 2104482, https://doi.org/10.1002/smll.202104482.
[10] G. Lee, Q. Wei, Y. Zhu, Emerging wearable sensors for plant health monitoring, Adv. Funct. Mater. 31 (2021) 2106475, https://doi.org/10.1002/adfm.202106475.
[11] Z. Li, J. Zhou, T. Dong, Y. Xu, Y. Shang, Application of electrochemical methods for the detection of abiotic stress biomarkers in plants, Biosens. Bioelectron. 182 (2021) 113105, https://doi.org/10.1016/j.bios.2021.113105.
[12] Y. Li, H. Xu, C. Han, Y. Bai, Y. Wang, H. Yu, W. Song, Z. Sun, Plant-wearable sensors for intelligent forestry monitoring, Adv Sustain Syst 7 (2023) 2200333, https://doi.org/10.1002/adsu.202200333.
[13] M.C.Y. Ang, T.T.S. Lew, Non-destructive technologies for plant health diagnosis, Front. Plant Sci. 13 (2022) 884454, https://doi.org/10.3389/fpls.2022.884454.
[14] A. Mohammad-Razdari, D. Rousseau, A. Bakhshipour, S. Taylor, J. Poveda, H. Kiani, Recent advances in E-monitoring of plant diseases, Biosens. Bioelectron. 201 (2022) 113953, https://doi.org/10.1016/j.bios.2021.113953.
[15] Y. Lu, G. Yang, Y. Shen, H. Yang, K. Xu, Multifunctional flexible humidity sensor systems towards noncontact wearable electronics, Nano-Micro Lett. 14 (2022) 150, https://doi.org/10.1007/s40820-022-00895-5.
[16] S.M.Z.A. Naqvi, Y. Zhang, M.N. Tahir, Z. Ullah, S. Ahmed, J. Wu, V. Raghavan, M. I. Abdulraheem, J. Ping, X. Hu, J. Hu, Advanced strategies of the in-vivo plant hormone detection, TrAC, Trends Anal. Chem. 166 (2023) 117186, https://doi.org/10.1016/j.trac.2023.117186.
[17] S. Zhou, J. Zhou, Y. Pan, Q. Wu, J. Ping, Wearable electrochemical sensors for plant small-molecule detection, Trends Plant Sci. 29 (2024) 219–231, https://doi.org/10.1016/j.tplants.2023.11.013.
[18] M. Ikram, S. Ameer, F. Kulsoom, M. Sher, A. Ahmad, A. Zahid, Y. Chang, Flexible temperature and humidity sensors of plants for precision agriculture: current challenges and future roadmap, Comput. Electron. Agric 226 (2024) 109449, https://doi.org/10.1016/j.compag.2024.109449.
[19] Y. Faqir, A. Qayoom, E. Erasmus, M. Schutte-Smith, H.G. Visser, A review on the application of advanced soil and plant sensors in the agriculture sector, Comput. Electron. Agric. 226 (2024) 109385, https://doi.org/10.1016/j.compag.2024.109385.
[20] W. Liu, Z. Zhang, X. Geng, R. Tan, S. Xu, L. Sun, Electrochemical sensors for plant signaling molecules, Biosens. Bioelectron. 267 (2025) 116757, https://doi.org/10.1016/j.bios.2024.116757.
[21] C. Kuruppuarachchi, F. Kulsoom, H. Ibrahim, H. Khan, A. Zahid, M. Sher, Advancements in plant wearable sensors, Comput. Electron. Agric. 229 (2025) 109778, https://doi.org/10.1016/j.compag.2024.109778.
[22] T.S. Martins, S.A.S. Machado, O.N. Oliveira, J.L. Bott-Neto, Optimized paper-based electrochemical sensors treated in acidic media to detect carbendazim on the skin of Apple and cabbage, Food Chem. 410 (2023) 135429, https://doi.org/10.1016/j.foodchem.2023.135429.
[23] 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, P.A. Raymundo-Pereira, Wearable sensors made with solution-blow spinning poly(lactic acid) for non-enzymatic pesticide detection in agriculture and food safety, Biosens. Bioelectron. 199 (2022) 113875, https://doi.org/10.1016/j.bios.2021.113875.
[24] S.C. Teixeira, N.O. Gomes, M.L. Calegaro, S.A.S. Machado, T.V. de Oliveira, N. de Fátima Ferreira Soares, P.A. Raymundo-Pereira, Sustainable plant-wearable sensors for on-site, rapid decentralized detection of pesticides toward precision agriculture and food safety, Biomater. Adv. 155 (2023) 213676, https://doi.org/10.1016/j.bioadv.2023.213676.
[25] F. Zhao, J. He, X. Li, Y. Bai, Y. Ying, J. Ping, Smart plant-wearable biosensor for in-situ pesticide analysis, Biosens. Bioelectron. 170 (2020) 112636, https://doi.org/10.1016/j.bios.2020.112636.
[26] Q. Zhang, S. Ma, W. Meng, Y. Zheng, L. Yin, H. Wang, H. Shi, K. Zhang, S. Su, Smartphone-based plant-wearable microfluidic sensor with self driven electrolyte for in-situ detection of methyl parathion, Sens Actuators B Chem 418 (2024) 136254, https://doi.org/10.1016/j.snb.2024.136254.
[27] V. Caratelli, G. Fegatelli, D. Moscone, F. Arduini, A paper-based electrochemical device for the detection of pesticides in aerosol phase inspired by nature: a flower-like origami biosensor for precision agriculture, Biosens. Bioelectron. 205 (2022) 114119, https://doi.org/10.1016/j.bios.2022.114119.
[28] L.J. Sun, Q.M. Feng, Y.F. Yan, Z.Q. Pan, X.H. Li, F.M. Song, H. Yang, J.J. Xu, N. Bao, H.Y. Gu, Paper-based electroanalytical devices for in situ determination of salicylic acid in living tomato leaves, Biosens. Bioelectron. 60 (2014) 154–160, https://doi.org/10.1016/j.bios.2014.04.021.
[29] S.A. Perdomo, D.P. Valencia, G.E. Velez, A. Jaramillo-Botero, Advancing abiotic stress monitoring in plants with a wearable non-destructive real-time salicylic acid laser-induced-graphene sensor, Biosens. Bioelectron. 255 (2024) 116261, https://doi.org/10.1016/j.bios.2024.116261.
[30] D. Liu, M. Li, H. Li, C. Li, G. Wang, P. Li, B. Yang, Core-shell Au@Cu2O-graphene-polydopamine interdigitated microelectrode array sensor for in situ determination of salicylic acid in cucumber leaves, Sens Actuators B Chem 341 (2021) 130027, https://doi.org/10.1016/j.snb.2021.130027.
[31] A. Bukhamsin, A. Ait Lahcen, J.D.O. Filho, S. Shetty, I. Blilou, J. Kosel, K. N. Salama, Minimally-invasive, real-time, non-destructive, species-independent phytohormone biosensor for precision farming, Biosens. Bioelectron. 214 (2022) 114515, https://doi.org/10.1016/j.bios.2022.114515.
[32] Z. Wang, L. Xue, M. Li, C. Li, P. Li, H. Li, Au@SnO2-vertical graphene-based microneedle sensor for in-situ determination of abscisic acid in plants, Mater. Sci. Eng. C 127 (2021) 112237, https://doi.org/10.1016/j.msec.2021.112237.
[33] H. Li, C. Wang, X. Wang, P. Hou, B. Luo, P. Song, D. Pan, A. Li, L. Chen, Disposable stainless steel-based electrochemical microsensor for in vivo determination of indole-3-acetic acid in soybean seedlings, Biosens. Bioelectron. 126 (2019) 193–199, https://doi.org/10.1016/j.bios.2018.10.041.
[34] Y. Zhang, M. Li, H. Li, A vertical/horizontal graphene-based microneedle plant sensor for on-site detection of indole-3-acetic acid in vegetables, Talanta 283 (2025) 127114, https://doi.org/10.1016/j.talanta.2024.127114.
[35] J. Gao, H. Li, M. Li, G. Wang, Y. Long, P. Li, C. Li, B. Yang, Polydopamine/graphene/MnO2 composite-based electrochemical sensor for in situ determination of free tryptophan in plants, Anal. Chim. Acta 1145 (2021) 103–113, https://doi.org/10.1016/j.aca.2020.11.008.
[36] L. Yang, Y. Ma, J. Ye, In vivo detection of L-tryptophan in tomatoes using multi-walled carbon nanotubes and poly (sulfosalicylic acid) film modified graphite rod electrode, Biosens. Bioelectron. X 9 (2021) 100086, https://doi.org/10.1016/j.biosx.2021.100086.
[37] Y. Lin, L. Yang, Y. Ma, J. Ye, Construction of minitype glutamate sensor for in vivo monitoring of L-glutamate in plant, Microchem. J. 188 (2023) 108505, https://doi.org/10.1016/j.microc.2023.108505.
[38] S.A. Perdomo, E. De la Paz, R. Del Caño, S. Seker, T. Saha, J. Wang, A. Jaramillo-Botero, Non-invasive in-vivo glucose-based stress monitoring in plants, Biosens. Bioelectron. 231 (2023) 115300, https://doi.org/10.1016/j.bios.2023.115300.
[39] R. Pandey, O. Teig-Sussholz, S. Schuster, A. Avni, Y. Shacham-Diamand, Integrated electrochemical chip-on-plant functional sensor for monitoring gene expression under stress, Biosens. Bioelectron. 117 (2018) 493–500, https://doi.org/10.1016/j.bios.2018.06.045.
[40] H. Ibrahim, S. Moru, P. Schnable, L. Dong, Wearable plant sensor for in situ monitoring of volatile organic compound emissions from crops, ACS Sens. 7 (2022) 2293–2302, https://doi.org/10.1021/acssensors.2c00834.
[41] H. Chen, S. Zhou, J. Chen, J. Zhou, K. Fan, Y. Pan, J. Ping, An integrated plant glucose monitoring system based on microneedle-enabled electrochemical sensor, Biosens. Bioelectron. 248 (2024) 115964, https://doi.org/10.1016/j.bios.2023.115964.
[42] T. Dotan, A. Jog, K. Kadan-Jamal, A. Avni, Y. Shacham-Diamand, In vivo plant bio-electrochemical sensor using redox cycling, Biosensors. 13 (2023) 219, https://doi.org/10.3390/bios13020219.
[43] P. Wang, W.C. Liu, C. Han, S. Wang, M.Y. Bai, C.P. Song, Reactive oxygen species: multidimensional regulators of plant adaptation to abiotic stress and development, J. Integr. Plant Biol. 66 (2024) 330–367, https://doi.org/10.1111/jipb.13601.
[44] K. Liu, B. Luo, L. Zhang, P. Hou, D. Pan, T. Liu, C. Zhao, A. Li, Flexible and wearable sensor for in situ monitoring of gallic acid in plant leaves, Food Chem 460 (2024) 140740, https://doi.org/10.1016/j.foodchem.2024.140740.
[45] G. Ai, Y. Zhou, H. Zhang, Q. Wei, B. Luo, Y. Xie, C. Wang, X. Xue, A. Li, Ultrasensitive molecular imprinted electrochemical sensor for in vivo determination of glycine betaine in plants, Food Chem 435 (2024) 137554, https://doi.org/10.1016/j.foodchem.2023.137554.

[46] C. Zhang, X. Wu, S. Yao, Y. Shao, C. Zhang, S. Zhou, J. Ping, Y. Ying, An implantable and self-powered sensing system for the in vivo monitoring of dynamic H2O2 level in plants, Engineering (2024), https://doi.org/10.1016/j.eng.2023.11.021.
[47] G. Chu, S. Yu, Y. Wang, W. Zhang, B. Xue, J. Huang, Z. Wang, J. Luo, X. Sun, M. Li, A wearable electrochemical sensor for the monitoring of neonicotinoid insecticides, salicylic acid and the pH in plant guttation, Chemical Engineering Journal 498 (2024) 155340, https://doi.org/10.1016/j.cej.2024.155340.
[48] M. Parrilla, A. Steijlen, R. Kerremans, J. Jacobs, L. den Haan, J. De Vreese, Y. Van Noten Géron, P. Clerx, R. Watts, K. De Wael, Wearable platform based on 3D-printed solid microneedle potentiometric pH sensor for plant monitoring, Chemical Engineering Journal 500 (2024) 157254, https://doi.org/10.1016/j.cej.2024.157254.
[49] M. Parrilla, A. Sena-Torralba, A. Steijlen, S. Morais, Á. Maquieira, K. De Wael, A 3D-printed hollow microneedle-based electrochemical sensing device for in situ plant health monitoring, Biosens. Bioelectron. 251 (2024) 116131, https://doi.org/10.1016/j.bios.2024.116131.
[50] Z. Yu, G. Cai, X. Liu, D. Tang, Pressure-based biosensor integrated with a flexible pressure sensor and an electrochromic device for visual detection, Anal. Chem. 93 (2021) 2916–2925, https://doi.org/10.1021/acs.analchem.0c04501.
[51] D. Wu, J. Tang, Z. Yu, Y. Gao, Y. Zeng, D. Tang, X. Liu, Pt/Zn-TCPP nanozyme-based flexible immunoassay for dual-mode pressure-temperature monitoring of low-abundance proteins, Anal. Chem. 96 (2024) 8740–8746, https://doi.org/10.1021/acs.analchem.4c01059.
[52] Z. Yu, Y. Tang, G. Cai, R. Ren, D. Tang, Paper electrode-based flexible pressure sensor for point-of-care immunoassay with digital multimeter, Anal. Chem. 91 (2019) 1222–1226, https://doi.org/10.1021/acs.analchem.8b04635.
[53] Z. Yu, G. Cai, P. Tong, D. Tang, Saw-toothed microstructure-based flexible pressure sensor as the signal readout for point-of-care immunoassay, ACS Sens. 4 (2019) 2272–2276, https://doi.org/10.1021/acssensors.9b01168.
[54] W. Tang, J. Wu, Y. Ying, Y. Liu, Writing sensors on solid agricultural products for in situ detection, Anal. Chem. 87 (2015) 10703–10707, https://doi.org/10.1021/acs.analchem.5b02558.