Review—Recent Advances in Nanosensors for Precision Agriculture

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Abstract:

Accurate assessment of plant health conditions across thousands of crops is a challenging undertaking in high density indoor farming as the environmental conditions experienced by individual plants can be very different. Manually inspecting visible symptoms of plant diseases is also not a feasible method because the process is time-consuming and human evaluations are subjective. Compared with traditional bulky sensors, nanosensor-based array can be seamlessly attached onto the plants to identify the onset and type of stress in-vivo via the detection of the plant signaling molecules triggered by plant stress. Most review articles about nanosensors are focused on the working mechanisms, fabrication processes, and device architectures. This review aims at highlighting how nanotechnology can introduce additional value to sensing applications for precision farming, together with the adoption of nanosensors in the current agricultural sector. Further efforts in understanding the applications of nanosensors in a safe and sustainable agriculture is also addressed.

Introduction

The global urban population is expected to grow by 2.5 billion between 2018 and 2050.[1] To secure food demand, we need to revolutionize urban farming into precision agriculture with an improved management practice. Precision agriculture is a farming concept applying advanced technologies, IoT, and big data to improve crop productivity with minimized environmental impact. In particular, the development of vertical indoor farming can reduce climate volatilities on crop yield and reduce carbon footprint by bringing farming solutions closer to urban areas.

For a sustainable agriculture, it is imperative to develop emerging technologies further to stimulate crop yield without over-consuming resources and inducing pollution. Sensors have emerged as efficient tools to render crop cultivation in a more sustainable way by reducing the dependence of agricultural chemicals needed for maintaining crop growth and health. According to the Artemis State of Indoor Farming Report 2016, 90% of the farmers believe that crop yield can be increased with farm data analytics.[2] Sensors, data analytics and LEDs are highly ranked by farmers as promising technologies to be invested for low-cost and high-yield indoor farming.[3] Indeed, smart indoor farming industry has rapidly developed with the use of sophisticated sensor systems, IoT technology and data analytics to increase crop yield, and reduced fertilizer use. Besides, the issue of pesticide overuse and heavy metal ion contamination is gaining increasing attention in the agriculture field. It is imperative to establish health surveillance system to monitor the plant uptake of these contaminants and bioavailability in the soil. With recent advancements in on-site sensing strategies, enforcing the inherent safety constraints to prevent heavy metal accumulation and pesticide residues in agricultural ecosystem has become more feasible.[4-7] Based on the data collected through these sensing strategies, preventive measures can be taken to reduce the risk to human health associated with the ingestion of contaminated crops. Farmers can thus make timely data-driven decisions to optimize crop yield and health based on the sensor data within the centralized agricultural control system.

Current status

Overview.—Using sensors, the aerial environment (air temperature, humidity, CO_2 concentration, air flow and incident irradiance) and the root environment (pH, electrical conductivity, temperature, mineral nutrients and dissolved oxygen in the irrigation water) for plant growth can be monitored in real-time. The sensor data can be consolidated and analyzed on top of the existing growth recipes for efficient farm management control. For example, the pH level of the irrigation water and nutrient solution are constantly regulated in a narrow range (5.8 to 6.4) in order to promote the nutrient uptake for carrot growth.[8] By installing the pH sensors in the irrigation pipes or growth chamber, the sensor data can be used to drive the environmental control system through the feedback loop that automatically injects mineral acids/bases and fertilizer to maintain the targeted pH and nutrient levels. Thus, the use of precision sensors for indoor farming is essential to facilitate the optimum maturity and crop productivity with less demand for resources (e.g. fertilizers).

Nanosensors can be also classified as precision sensors with at least one of its dimensions being smaller than 100 nm, and demonstrating an ultimate detection limit down to a single-molecule level of the detection target. Nanosensors can find application in the agricultural sector through various means, such as by being injected into plant tissue, printed onto plants, or integrated into larger devices that utilize the unique properties of nanomaterials to sense and detect specific signals at the nanoscale. Contrary to bulky precision sensors, the injectable and printable nanosensors have shown unprecedented resolution and reproducibility in detecting the pollutants created from the agricultural production activities (e. g. atmospheric ammonia),[9] moisture, soil pH and fertilizer level.[10] There have been a few comprehensive reviews discussing about the properties and applications of nanosensors for monitoring the planting environment and health of plants.[11-21] The high sensitivity, specificity, stability and accuracy followed by the rapid response rate make nanosensors more useful for smart agriculture over conventional sensors due to their higher surface to volume ratio, and faster electron transfer kinetics.[12]

With the technological revolution being made in nanotechnology, nanosensors have been developed to play a significant role in the advancement of agriculture. The application of nanosensors can revolutionize agriculture by providing rapid updates in the growing environment, such as air flow, air humidity, carbon dioxide, temperature, pH and dissolved oxygen in water. Nanosensor-based monitoring systems can prevent crop loss and excessive use of fertilizers via rapid response and highly sensitive sensors in adjusting the agricultural environment for optimal plant growth. Nowadays, different nanomaterials have been seamlessly integrated with conventional devices for monitoring farming conditions, such as reduced graphene oxide (rGO) nanosheets,[22] graphene oxide (GO) nanosheets,[22] zinc oxide (ZnO) nanorods,[23] manganese oxide (MnO) doped carbon nanodots,[24] carbon nanotubes (CNTs),[25-29] copper (Cu) nanoparticles[26] etc. **Table I** summarizes different detection targets that have been reported to be monitored by nanosensors.[22-33] A nanostructure consisting of rGO/GO/rGO was used to detect humidity changes which showed a fast response time (1.9 s), recovery time (3.9 s), wide detection range (6.3-100 %) and good long-term stability (>1 year). This sensor has shown its potential adoption in real-time humidity monitoring with a smart phone based on IoT and data analytics.[22] Detection of pH in water using ZnO nanorods-based interdigitated electrodes has also shown a high sensitivity of 1.06 nF/pH in the range of pH 4−10.[23]

Table I. Different detection targets monitored by current state of the art nanosensors[a].

Detection Target	Nanomaterial	Detection Limit	Response Time	Detection Range	Type of Study	Ref
Air Flow	CNTs	0.05 m/s	1.3s	0.05 – 7 m/s	Ex-vivo	[34]
Air Humidity	rGO/GO/rGO	6.3%	1.9s	6.3 – 100%	Ex-vivo	[22]
Carbon dioxide	Ag-doped $BaTiO_3$-CuO	76.3% for 1000 ppm	300 – 360s	300 – 1000 ppm	Ex-vivo	[31]
Temperature	MnO_x-doped carbon NDs	–	–	10 – 60 °C	In-vivo	[24]
pH	ZnO NRs	1.06 nF/pH	1s for acidic, 10s for alkaline	pH 4 – 10	In-vivo	[23]
Dissolved oxygen	Au-CrO_2 NPs	–	–	7.8 – 22 mg/L	Ex-vivo	[32]
DMMP	SWCNTs-Graphite	5 ppm	5s	–	Ex-vivo	[28]
Nitrate	CNTs/Cu NPs	4 nM	15s	1 μM – 5 x 10^{-3} M	Ex-vivo	[26]
Potassium	Silica NPs-based	2.8 μM	<1s	0-150 mM	In-vivo	[35]
Phosphate	Mn-doped ZnTe/ZnSe QDs	0.2 μmol/L	–	0.67 – 50 μmol/L	Ex-vivo	[33]

Ethylene	Porous SWCNTs	0.5 ppm	–	0.5 – 50 ppm	Ex-vivo	[27]
Hydrogen peroxide	SWCNTs	10 μM	–	10 – 100 μM	In-vivo	[36]
Nitric oxide	SWCNTs	300 nM	1.1s	0.2 – 20 μM	In-vivo	[25]
Hydrogen peroxide	AuPtNPs/MoS$_2$	0.01 mM	–	0.05–3.14 mM	In-vivo	[37]

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[a] Abbreviations: CNTs, carbon nanotubes; rGO, reduced graphene oxide; GO, graphene oxide; SWCNTs, single walled carbon nanotubes; Cu NPs, copper nanoparticles; NPs, nanoparticles; Mn-doped ZnTe/ZnSe QDs, manganese-doped zinc telluride/zinc selenide quantum dots; ZnO NRs, zinc oxide nanorods; DMMP, dimethyl methylphosphonate; Ag-doped BaTiO$_3$-CuO, Silver-doped barium titanate-copper oxide; MnO$_x$-doped carbon NDs, manganese-doped carbon nanodots; Au-CrO$_2$ NPs, gold-chromium nanoparticles; AuPtNPs/MoS$_2$, gold-platinum nanoparticles coated molybdenum disulfide.

Contrary to traditional analytical methods involving the use of bulky sensors, nanosensors can also be printed on leaves with a small radius of curvature (~100 μm)[38] and injected into plant tissues[24, 25, 35, 39]. For example, highly sensitive gas sensors based on single-walled CNTs-Graphite were printed on living plants for rapid sensing of toxic dimethyl methylphosphonate (DMMP) gas. Such wearable nanosensors can be operated with low power consumption and high sensitivity in parts per million (ppm) through the use of adequate surface functionalization on the nanomaterials.[38] MnO-doped carbon nanodots were injected into plants for in-vivo measurement of the temperature change inside the plants.[24] Consequently, this study paves the way to develop nanoscaled thermometers for real-time tracing of local microclimate inside plants. Indeed, it is essential to develop a platform to continuously monitor the localized conditions inside living plants in order to improve the growth yield and quality. A biodegradable nanosensor which can simultaneously measure three intracellular parameters (temperature, pH and oxygen concentration) in living cells has been demonstrated.[40] This compact multisensory platform will provide an accurate in-situ tracing in the planting environment.

Macronutrients, such as nitrogen, phosphate and potassium species, are indispensable for plant growth. Conventional monitoring methods rely on sensing the macronutrient concentration in soil, water or nutrient solution. However, the measurements may not indicate the assimilation values in the plants as the nutrient uptake will be affected by root membrane permeability[41] and rooting volume.[42] Indeed, an accurate in-situ traceability for nutrients in plants is essential for sustainable agriculture so that unintentional overdose of nutrients/fertilizers during the course of cultivations can be avoided. Furthermore, it is challenging to detect nitrogen species based on traditional sensors, due to their short lifetimes and rapid diffusivities.[43] To overcome such problems, a miniaturized sensor probe based on CNTs/Cu nanoparticles has been developed to sense nitrate with high sensitivity (80.62×10^{-6} nm/M), fast response time (15 s) and wide operating range (10^{-6} M – 5×10^{-3} M).[26] The combination of CNTs and Cu nanoparticles with high charge density, large surface area and unique catalytic properties produces a versatile platform for the detection of nitrates. An in-vivo study about the rapid and quantitative detection of potassium cations based on mesoporous silica nanoparticles was constructed.[35] By coating a potassium-specific filter membrane on the nanoparticles, the sensitivity and selectivity of the nanosensors can be amplified, thus allowing the detections of extremely low potassium content in living cells.

Monitoring every growth stage of plants is also an important aspect for a sustainable agriculture. To date, the method to monitor the plant and fruit development is still limited to the use of active imaging systems installed on-site at the plant, which allow the detection of the variables of plant growth such as shoot length, stem diameter and plant morphology.[44] Relying on traditional imaging methods is very challenging to pinpoint the precise time for harvesting . Taking advantage of the ultimate detection limit of CNTs-based nanosensors down to a single-molecule level of the detection target,[25] researchers have developed single-walled CNTs-based nanosensors to detect the low concentration of ethylene in ppm level, a plant hormone that acts as a key indicator of the onset of fruit development, released from different fruits (banana, avocado, apple, pear and oranges).[27] This type of nanosensor is extremely sensitive to ethylene gas released by spoiled fruit. Such a sensory system will give a clear indication once the fruit is ready to be harvested.

The accurate evaluation of crop health in high density indoor farm remains a challenge due to the significant disparities in the environmental conditions experienced by each plant. The inspection of visible symptoms of plant diseases is also not a viable approach due to its time-consuming nature and human evaluations are subjective. Nanosensors have been utilized to identify the onset and type of stress in-vivo by detecting the plant signaling molecules through the seamless contacts on plant surface.[37, 45-47] For example, hydrogen peroxide (H_2O_2) is a key signal molecule generated by environment- and pathogen- related stresses.[39, 48] Taking advantage of the highly stretchable property of CNTs, a flexible sensor platform based on functionalized single-walled CNTs was developed to monitor the concentration of H_2O_2 in real-time.[49] This type of nanosensor can detect and indicate how plants respond to different type of stresses, such as light stress, heat stress, wounding and pathogen infection, based on the H_2O_2 signals, as well as applicable for different species (e.g. spinach, lettuce and watercress). The onset of stresses can be remotely reported with macroscopic imaging devices which provide a feasible sensing way to locate and differentiate the plant stress before the symptoms become visible. High-performance electrochemical nanosensors based on flexible molybdenum disulfide (MoS_2) electrodes were also demonstrated for the detection of H_2O_2 (Figure 1).[37] Without any auxiliary condition, the two-dimensional nature of metallic MoS_2 papers allow the spontaneous growth of noble metal alloy nanoparticles (AuPtNPs) with high catalytic activity. The excellent mechanical properties provided from the flexible AuPtNPs/MoS_2 electrode promote the development of wearable detection system with high sensitivity/stability in a wide linear range for real-time inspection of plant physiological condition.

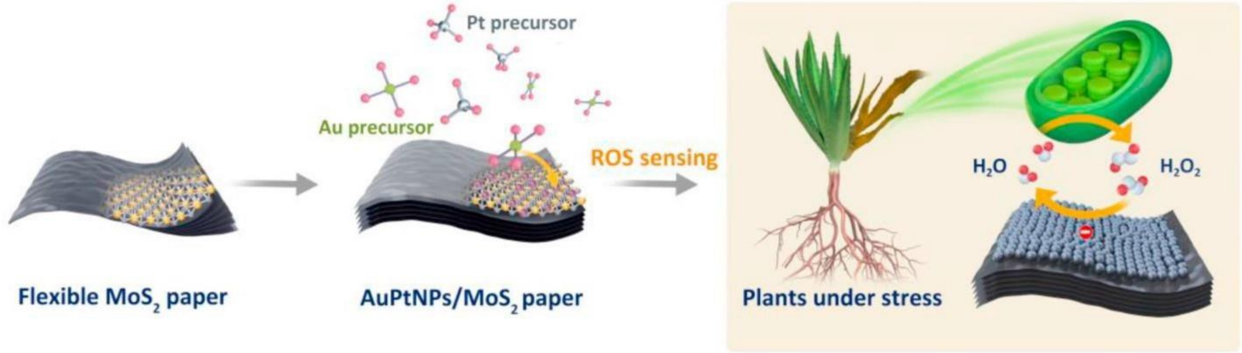

Figure 1. Schematic depiction of the spontaneous growth of AuPt nanoparticles (AuPtNPs) on paper-based molybdenum disulfide (MoS_2) and the H_2O_2 sensing in plant extract. Adapted with permission from Ref. 37, Copyright 2020, Elsevier B.V. information.

Commercial Adoption of Nanosensors in Agricultural Sector

According to Market Research Future, the Global Nano Sensors Market is expected to grow from USD 870 million in 2023 to USD 1,770 million by 2030 at a compound annual growth rate of 9.18 %.[50] Nanosensor market includes the application of nanotech devices for energy, healthcare, chemical manufacturing, defense technology and personal electronics. Currently, a number of industries are working on the development of nanosensors using metal oxide nanoparticles and carbon nanotubes to track the important elements for cultivation. For example, innovators in SmartCultiva have developed the nanosensing system that traces real-time humidity, air/water temperature, light intensity, carbon dioxide level and soil moisture accurately.[51] The analysis of these indoor farm parameters allows growers to locate the deviations from intended set points with a fully automated growing control system, hence, avoiding loss of crop quality and yield. Computer chip maker Intel has installed a big wireless sensor node to periodically monitor the temperature in a USA vineyard.[52] The chemical nanosensors developed in Razzberry can measure small variations in pH (e.g. as precise as 0.05 pH units) by integrating with conventional solid state electrode. In order to develop erosion resistant electrodes for soil analysis, titanium oxide nanoparticles were coated on solid state electrodes to increase the reliability of pH measurement.[53]

Spanish company NT sensors incorporates carbon nanotubes as the transducer in ion selective electrodes (ISEs).[54] The merit of using carbon nanotubes is that it can lower the detection limit of nanosensors down to a single molecule level.[55, 56] The large surface-to-volume ratio with high charge transfer capacity of carbon nanotubes increases the ion detection sensitivity of ISEs.[57] Their carbon nanotube-based water quality meters can offer a rapid and reliable measurements of 11 parameters (7 types of ions, nutrients, pH, EC and water hardness) simultaneously. Ireland-based CleanGrow has also applied a layer of carbon nanotubes as the transducing element in their sensor probes for monitoring the level of nutrients (e.g. nitrate, sodium, etc) in soil or water.[58] Taking advantage of the high electrical conductivity of the carbon nanotubes (2000 times more conductive than copper), the detection sensitivity can be significantly amplified with the nanotube-based transducer compared with conventional copper transducer.

Potential challenges and future prospects

Despite high-performance nanosensors show promising advancements, their active integration into the agricultural sector still faces challenges. Nanosensors have yet to be tested in real scenarios where the sensing performance may be affected by weather conditions. To evaluate on-site sensor performance in various specific environments, it is crucial for nanosensor companies to collaborate with regulatory agencies closely, particularly with regard to safety measures. In fact, the inherent safety concerns about the application of nanosensors with crops must be carefully addressed for a safe and sustainable agriculture. Analytical methods must be developed to validate the effects of the nanomaterial usage and disposal in the ecosystems. Further development is still required to develop the light, wearable and stretchable nanosensors with seamless integrated contacts with living plants for the real-time in-vivo studies. New design and miniaturization of multi-sensing platform will offer the promise of practical applications in monitoring various plant growth parameters simultaneously.

Conclusion

Nanosensors play a vital role in the precision agriculture and being reviewed in terms of their distinct working mechanism, manufacturing methods and device configuration in the literature. In contrast, this review highlights recent representative nanosensors specifically designed for monitoring localized conditions within living plants and planting environment for improved crop yield, quality and safety. Besides, the commercial exploitation of the nanosensors, potential challenges and future prospects for the safe and sustainable agriculture are also addressed here. We envision that the highly sensitive and multi-functional nanosensor platform will pave a way to monitor the plant health and planting environment for sustainable and safe crop production. By integrating multi-functional nanosensors with multispectral image visualization systems with a library of algorithms, automatic identification of plant stress will be advanced through the growing period. Coupled with IoT-driven real-time regulation in planting system, precision agriculture with increased crop productivity with minimized resource needs will be possible. Further efforts in understanding the biocompatibility of nanosensors in both crop safety and environmental impact must be verified in the near future.

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