chemosensors

Review

Micro/Nano Soft Film Sensors for Intelligent Plant Systems: Materials, Fabrications, and Applications

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Abstract: Being abundant as natural intelligence, plants have attracted huge attention from researchers. Soft film sensors present a novel and promising approach to connect plants with artificial devices, helping us to investigate plants' intelligence further. Here, recent developments for micro/nano soft film sensors that can be used for establishing intelligent plant systems are summarized, including essential materials, fabrications, and application scenarios. Conductive metals, nanomaterials, and polymers are discussed as basic materials for active layers and substrates of soft film sensors. The corresponding fabrication techniques, such as laser machining, printing, coating, and vapor deposition, have also been surveyed and discussed. Moreover, by combining soft film sensors with plants, applications for intelligent plant systems are also investigated, including plant physiology detection and plant-hybrid systems. Finally, the existing challenges and future opportunities are prospected.

Keywords: soft film sensors; intelligent plant systems; plant intelligence

Citation: Jiang, Q.; Chai, Z.; Zong, Z.; Hu, Z.; Zhang, S.; Wu, Z. Micro/Nano Soft Film Sensors for Intelligent Plant Systems: Materials, Fabrications, and Applications. *Chemosensors* **2023**, *11*, 197. https://doi.org/10.3390/chemosensors11030197

Academic Editor: Boris Lakard

Received: 10 February 2023
Revised: 15 March 2023
Accepted: 17 March 2023
Published: 19 March 2023

1. Introduction

As an essential part of the ecosystem, plants play irreplaceable roles in the global carbon cycle [1], ecological balance [2], and climate adjustment [3]. In the meantime, plants have inseparable relationships with humankind. In addition to being our primary food source, plants are essential to our daily lives as they offer us industrial resources, purify the air, and heal our emotions. Since most plants lack obviously visible movements, we always tend to regard/treat them as passive creatures, lacking effective intelligence and interactions with us. We did not begin to recognize and gradually expose the remarkable intelligence hidden behind plants' inconspicuous behaviors until very recently [4].

The intelligence of plants can be shown in three aspects [5,6]: (1) Basic biological behavior. For instance, plants have developed particular sensory organs that can sense variations in their living environments, such as light intensity, temperature, humidity, and gravity. Based on their biological instincts, plants are able to take superior strategies for adapting to external environments, e.g., tip phototropism [7] and root hydrotropism [8]. (2) Reaction mechanisms. During long-term evolution, plants obtained various inducible defensive or predatory mechanisms for reacting to external stimulations [9,10]. For instance, the *Mimosa pudica* (also known as the shame plant) will close its leaves against insects in response to touch, vibration, and wind. The *Venus Flytrap*, whose traps have miniature antennae, is capable of precisely detecting and facilely catching insects. (3) Swarm intelligence, where a group of species coordinate and cooperate with each other to enhance their individual living ability, has also been widely seen in plants. For instance, certain plant species can distinguish between self and non-self roots to coordinate and compete for absorbing nutrients [11].

Currently, the investigation of plant intelligence is becoming a serious scientific endeavor, yet we still have not fully/symmetrically explored it. One of the grandest challenges is to build a connection between plants and human beings' worlds to investigate plants' intrinsic embodiment signals. Soft film sensors, whose active layer thickness features micro/nanoscale structures, show incredible potential in helping us to open the door to plant intelligence. Unlike traditional rigid sensors, soft film sensors possess unique flexibility, stretchability, and conformability that allows them to be directly attached to plant surfaces for real-time and individual/collective monitoring [12–14]. Most importantly, these sensors cause relatively little disturbance to plants' natural growth or phycological activities. With the help of soft film sensors, the complex biological signals of plants will excite the physiochemical change in active materials, which are then translated into digital ones that are compatible/interchangeable with various modern tools. Ultimately, they can be easily interpreted and widely spread over the world in forms that humans can easily understand. Therefore, combining soft film sensors with plants is one of the most promising ways to establish intelligent plant systems.

Plant physiology detection is one of the most important applications of intelligent plant systems. Soft film sensors can be integrated with plants to investigate plants' biological information to monitor and modulate various vital parameters related to growth, product quality, and living environments. According to these essential physiological data, we can establish intelligent plant management systems that supply suitable living environments for plants. Another important application scenario is plant-hybrid systems, where living plants are viewed as biological machines that replace artificial ones. As mentioned above, plants are amazing machines with abundant natural intelligence abilities. Based on soft film sensors, artificial intelligence techniques can be combined with plants to establish intelligent plant-hybrid systems.

In this article, we will review soft film-based micro/nano sensors for the development of intelligent plant systems (Figure 1). To build such a system technically, we first overview the essential materials of soft film sensors, including metals, nanomaterials, and polymers. To be compatible with plants, the specific materials of soft film sensors need to be selected and modified properly. Typical fabrication techniques for soft film sensors are then presented, with the main techniques including laser machining, printing, coating, and vapor deposition. Furthermore, we highlight two application scenarios of intelligent plant systems, including plant physiological detections and plant-hybrid systems. Finally, the existing challenges and new opportunities are discussed.

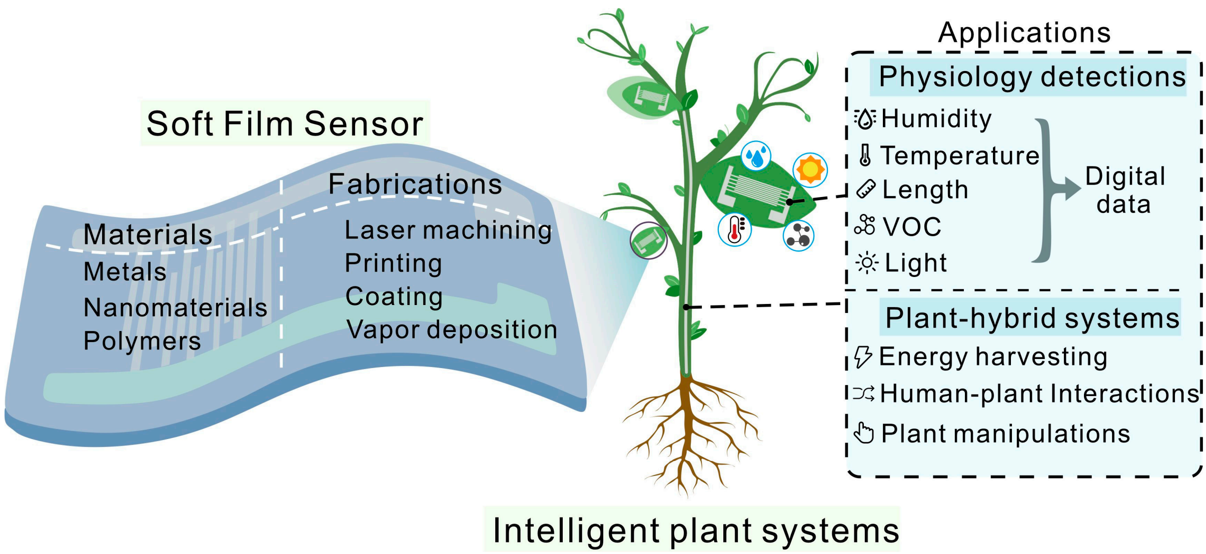

Figure 1. Overview of micro/nano soft film sensors for the establishment of intelligent plant systems.

2. Materials

Materials are the fundamental factor in micro/nano soft film sensors. As these sensors are attached to tender plant surfaces, soft materials should not only possess low stiffness, flexibility, and stretchability, but also need to consider other specific properties, including biocompatibility, permeability, and conformability. Moreover, modification and synthesis mechanisms are often necessary during material preparation to improve and develop innovative materials with new features and functionalities. We categorize common materials into the following three aspects: metals, nanomaterials, and polymers (Figure 2).

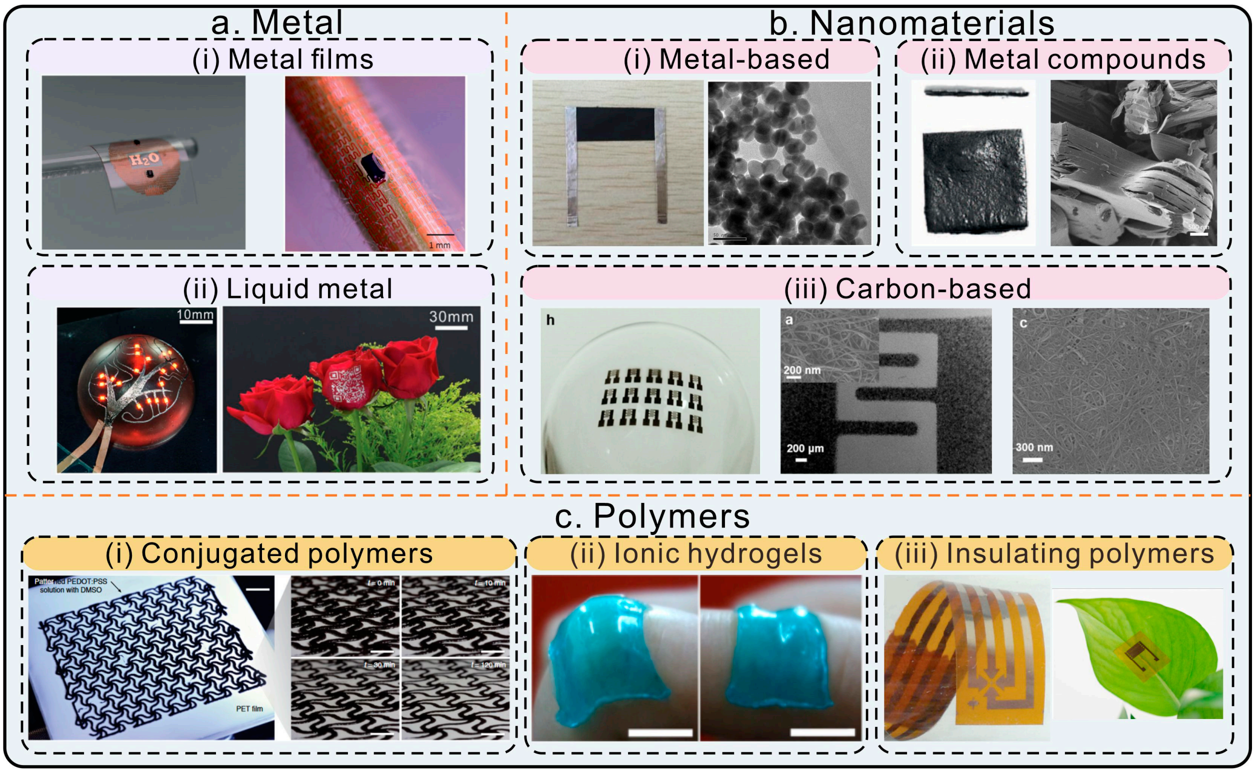

Figure 2. Materials for soft film sensors. (**a**) Metals for fabricating soft film sensors. (i) Metal film-based soft sensors for stem flow detection (reproduced with permission from [15], copyright © 2013, Wiley-VCH GmbH). (ii) Liquid metal-based soft electronics (reproduced with permission from [16], copyright © 2020, Wiley-VCH GmbH). Left, liquid metal traces on a hemispheroid. Right, liquid metal patterns on living rose flowers. (**b**) Nanomaterials. (i) Flexible strain sensors with silver nanoparticles as sensing materials (reproduced with permission from [17], open access Creative Commons CC-licensed 4.0, MDPI). (ii) MXene sheets and SEM images of multilayer MXene particles (reproduced with permission from [18], copyright © 2014, Macmillan Publishers Limited). (iii) Sprayed CNT interdigital electrodes and SEM images at different magnifications (reproduced with permission from [19], copyright © 2018, American Chemical Society). (**c**) Polymers. (i) Pure PEDOT:PSS hydrogel patterns (reproduced with permission from [20], copyright © 2019, Macmillan Publishers Limited). (ii) Tough, adhesive, self-healable, and transparent ionically conductive hydrogels as strain sensors (reproduced with permission from [21], copyright © 2019, American Chemical Society). (iii) Polyimide-encapsulated soft film sensors. Left, wearable magnetic field sensors based on polyimide film (reproduced with permission from [22], copyright © 2015, Wiley-VCH GmbH). Right, soft film sensor attached to the leaf surface (reproduced with permission from [23], copyright © 2020, Elsevier).

2.1. Metals

Conductive metals are probably the most common materials for soft film sensors owing to their excellent conductivity for electric signal transfer. Thus, common metals are further divided into two aspects to discuss: metal films and liquid metal.

2.1.1. Metal Films

Thin metal films (such as Ag, Cu, and Au) are common materials for soft film sensors owing to their high conductivity, high stability, and convenience. When these conductive metals' thicknesses become very thin (micro/nanometers), these metal films become structurally soft regardless of their intrinsic rigidity or mechanical properties. Bonding these metal films onto soft (e.g., polyimide film) or elastic (e.g., silicone rubber) substrates, metal-based circuits can obtain flexibility and stretchability, which allows them to be cyclically bent, stretched, and scratched.

Various circuit structure designs are proposed to decrease the stress concentration of metal circuits and enhance their conformabilities, such as serpentine interconnections and origami and kirigami designs [24]. When responding to the applied strain, these structures can rotate in a plane and buckle out of the plane, significantly reducing strain and the stiffness of metal film traces. Therefore, "island-bridge" structures have been widely presented for soft film sensors. By accommodating rigid functional components as "islands" that are connected by conductive bridges, soft devices possess high stretchability [25].

2.1.2. Liquid Metal

Owing to their unique physical properties, such as a low melting point, low toxicity, excellent fluidity, high electrical conductivity, and good thermal conductivity, gallium-based liquid metals (LMs) such as gallium–indium–tin alloy (e.g., Galinstan: $Ga_{68.5}In_{21.5}Sn_{10}$) and eutectic gallium–indium (e.g., EGaIn: $Ga_{75.5}In_{24.5}$) are wildly employed for the fabrication of soft film sensors [26]. Most of the time, LMs present a liquid state at room temperature, yet their melting point can be changed by adjusting the component proportions of metals [27].

LM is generally considered to be nontoxic or slightly toxic depending on the external environments, dosage, form, and doping materials [28]. Moreover, many in vitro and in vivo experiments have shown that LM has good biological safety [29]. Due to the low vapor pressure under normal conditions and limited solubility in water, LM vapor is theoretically unable to penetrate the cells of animals and plants to cause cytotoxicity. Therefore, LM has been widely utilized as a biomaterial in tumor therapy, drug delivery, skin electronics, and cryotherapy [30]. Even after directly printing LM circuits on bean sprouts and lotus leaves, these plants were able to maintain visually healthy growth separately after 11 days and 26 days [16,31]. Although there is insufficient evidence to show that LM has no negative effects whatsoever on plant health during long-term contact, we can keep a positive attitude when exploring the application of LM-based sensors for plants.

LM has very high surface tension (>700 mN/m), nearly about ten times that of water, making it tend toward a spherical morphology to reduce surface energy. When the LM is exposed to air, even with a ppm level of oxygen, the solid oxide skin (Ga_2O and Ga_2O_3) of LM instantaneously generates. The thin film oxide skin (~1–5 nm) lowers the interfacial tension and impacts LM's rheology [32]. Attributed to fluidity and low viscosity similar to that of water, unoxidized LM can flow easily without the constraint of the oxide shell. Additionally, the unoxidized LM has poor wettability between metal and non-metal surfaces. However, oxide-coated LM can help maintain its shape, which is important for patterning liquids. The oxide skin also acts as an adhesive bridge between LMs and various surfaces, such as elastomers, plastics, metals, and even plants. Particularly, plants have natural micro/nano-structured surfaces that present two main types of surfaces, hydrophilic and hydrophobic, while also presenting some that fall between. For hydrophilic and some hydrophobic surfaces, LM can easily be directly printed on them (e.g., stems of bean sprout) or helped by water (a high-surface-energy liquid) to pin onto the rough epidermal surface (e.g., flowers of rose and lily) [16]. However, some super-hydrophobic surfaces, e.g., lotus leaves, show extreme LM repellency. Such a character results in water and LM having difficulty wetting the surface of lotus leaves directly. In such a case, the introduction of a surfactant solution can significantly change the interfacial characteristics of lotus leaves and allow LM circuits to be printed on them [31].

Due to intrinsic liquidity, LM gains potentially infinite deformability that depends on the attached substrate. Encapsulated by stretchable elastomers, the LM circuits can maintain connections when highly strained by up to ~1000% due to ultra-stretchability [33]. The LM-based circuits contain robustness which can go through stretching, writing, bending, twisting, and even compressing. Moreover, LMs show remarkable softness and conformability to patterns on various surfaces, including two-dimensional (2D), three-dimensional (3D), static, and even dynamic surfaces. Owing to these unique properties, LM-based electronics can provide a gentle way to directly attach circuits to the tender surface of plants without rigid carrier films. Notably, LM-based circuits can co-exist with the rapid growth of plants (e.g., bean sprouts) and maintenance functions that are used to detect biological signals at high strain (over ~500%).

2.2. Nanomaterials

Nanomaterials cover a large number of materials that usually constitute a functional part of film sensors. These solid materials are naturally conductive or semi-conductive. They exhibit distinct physiochemical differences from their bulk materials and have excellent responses under the stimulation of potential, humidity, temperature, light, and specific gas molecules. Once the stimulation of interest is detected, the electrical property (e.g., conductivity and permittivity) of these materials or the ambient environment will change accordingly, which in turn changes the electrical signals to suggest the existence of stimulations. Proper modification and application of these materials endows sensors with many attractive functions for intelligent plant systems. However, the necessary packaging of these nanomaterials should be taken into serious consideration during material selection as potential adverse effects can impact plants. Plenty of nanomaterials influence the health of plants in a dose-dependent manner, and only appropriate doses of nanomaterials will be beneficial to the growth of plants. Moreover, nanomaterials can be easily absorbed by plants and gradually accumulate in them, which might lead to them finally invading the food chain and causing detrimental effects in humans. Thus, it is vital to consider phytotoxicity when designing film sensors. Several researchers have already summarized the impact of nanomaterials on plants, and readers can refer to their reviews for more details [34,35]. In this section, we will mainly discuss three categories of nanomaterials: carbon-based nanomaterials, metal nanomaterials, and metal compound nanomaterials.

2.2.1. Carbon Particles, Carbon Nanotubes, Graphene-Based Materials, and Graphite

These materials are frequently adopted as carbon skeleton nanomaterials. The allotropes of carbon possess very distinct physical appearances and good electrochemical properties that can be utilized in various stimulation detections [36,37].

Carbon particles are theoretically spheroidal materials with nanoscale size in all three dimensions, which can be practically categorized into 0D materials. Carbon particles, which are theoretically spheroidal, are categorized into 0D materials. Compared with the ideal 0D fullerenes that are expensive and hard to synthesize, carbon black is cheap and widely adopted in soft film sensors. Carbon particles are connected together by covalent bonds to form carbon black aggregates. Many of the aggregates are spheroidal, and others are irregularly shaped with branches. These aggregates can be small in size and are usually observed with a dimension of 10–100 nm [38]. Due to the nanoscale size and large area-to-volume ratio of carbon black particles, researchers have developed two different ways to overcome the fabrication difficulty of such high-surface-energy particles. A representative approach is to blend carbon black with polymer precursors and cure the composite for stretchable and conductive wires [17,39], which is a straightforward way to confine particles prior to their aggregation. Carbon black particles serve as conductive fillers in the elastomer matrix and create numerous conductive pathways for the transportation of electrons. The volume fraction and the particle size of carbon black particles dominate the percolated networks in the composite. Often, with a higher volume fraction, the smaller size will generally result in composites with lower resistance [24,40]. The carbon black/elastomer composite provides an easy yet useful way to prepare functional materials for both resistive and capacitive film sensors [41]. The carbon black/elastomer composite also provides an easy yet useful way of preparing functional materials for resistive film sensors. The other representative approach is to disperse carbon black particles in dispersant-activated liquids. For instance, carboxymethyl cellulose and polyvinyl alcohol (PVA) solutions have been reported to disperse carbon black and make it stable evenly [42,43]. Such a stable solution is then coated on a substrate to form a nano-structured carbon black-based conductive layer to measure strain.

Carbon nanotubes (CNTs) are high-aspect-ratio hollow tubes rolled up by a thin layer (or layers) of graphene sheets. The diameter of CNTs ranges from 1 nm to 100 nm, with their length ranging from several nanometers to tens of micrometers [36,37]. Single-walled carbon nanotube (SWCNTs) are rolled up by one layer of graphene sheets, and multi-walled carbon nanotubes (MWCNTs) are rolled up by multiple layers of graphene sheets. As the conductivity along the axis of CNTs is very high, CNTs are regarded as 1D materials. Similar to carbon particles, CNTs can be used as conductive fillers for resistive and capacitive sensors [44,45], as well as freestanding thin films for conductive or semi-conductive applications [19,46,47]. Although the processing of CNTs also faces the challenge of easy aggregation caused by strong Van der Waals interactions, researchers have developed a large amount of covalent and non-covalent functionalization methods to settle down this problem and impart desired properties to CNTs [48]. Furthermore, leveraging the non-covalent modification principle, CNTs can be used to detect the concentration of organic molecules in the air, which provide effective ways for plants to actively sense their ambient environment [47].

Graphene possesses exceptional electrical, thermal, and mechanical properties and is a single layer of well-structured carbon atoms [49]. Apart from the fact that graphene can be blended into various polymers to function as a conductive 2D filler [50], freestanding graphene and its derivatives play a more important role in sensing diverse molecules. Good electron mobility at room temperature, the large surface area provided by carbon atoms, and inherently low electrical noise make graphene a highly sensitive material to chemical environments [51]. For instance, laser-induced graphene has been widely utilized to fabricate the electrode of film sensors used for the quantification of pesticides [52], precipitation [53], and vaporized molecules [47]. In addition, graphene nanosheets have been applied to measure the relative humidity (RH) beneath leaves [54]. Water molecules absorbed by graphene serve as electron acceptors that attract electrons and increase the graphene sheet’s resistance, leading to water vapor detection. As a matter of fact, molecules that are able to either attract electrons or repel electrons can be detected quantitatively. Many kinds of molecules that can be used to monitor the state of plant growth or the ambient environment (such as CO, NO, and NO_2) are detectable substances [55,56].

Graphene oxide (GO), which has numerous oxygen functional groups on its surface, is an oxidized form of graphene. Due to the existence of oxygen functional groups, the electrons cannot move freely on the graphene, making GO an insulator [51]. However, most of these functional groups (e.g., -OH and -COOH) are hydrophilic, making GO an excellent active material for humidity sensing [57]. When water molecules are absorbed by GO, the GO can be dissolved and ionized to reduce the impedance of the electrical network, which ensures the detection of RH [58,59]. Hence, GO-based film sensors are good candidates for measuring transpiration from stomata, which in turn indicates the drought stress on plants [23,60]. Another graphene-based nanomaterial that is frequently adopted for chemical sensing is reduced graphene oxide (rGO). rGO, which has fewer functional groups than GO, is a thermally or chemically reduced substance of GO. Due to the incomplete reduction of functional groups, rGO possesses high conductivity as well as good chemical activity [36]. The detection of RH, temperature, and gas signals has been realized by rGO-based film sensors [19,42,61].

Graphite, as a typical 3D material, is another carbon nanomaterial stacked together by layers of graphene. Therefore, graphite is highly conductive and can likewise be filled into polymers for electrical modification. For instance, Tang et al. mixed graphite and chitosan solutions together to form conductive ink [62]. The ink is later directly written on an elastomer substrate for the resistive-based perception of plant growth. Moreover, the high conductivity of graphite makes it a decent material for electrodes. Combining graphite-based electrodes with a CNT-based functional part, an all-carbon-based film can be fabricated for organic molecule detection [47].

2.2.2. Metal-Based Nanomaterials

As it is well known, metals are widespread materials that can be used for the fabrication of electrodes and conductive materials. Based on the flexibility of serpentine metal wires and the stretchability of nanowire-based electrodes, thin film sensors can conform to the leaf surface and continuously monitor the physiological signals of plants [15,63]. Similarly, metal nanowires and metal nanoparticles can form percolated networks for the resistive sensing of strains [24].

Electrical conductivity is a fundamental property of metal nanomaterials and has been widely used. Apart from basic electrical properties, the chemical properties of metal nanomaterials are also fascinating. Because of the size effect of nanomaterials, these metal nanoparticles can significantly influence the catalysis of electrochemical reactions and the electron transfer process to improve the sensitivity of flexible plant sensors [64]. Frequently adopted materials include noble metallic nanomaterials such as palladium (Pd), gold (Au), silver (Ag), and platinum (Pt). These materials are usually adopted for the modification of other active materials, such as the aforementioned carbon-based materials. Due to the inertness of noble metallic nanomaterials, their introduction seldom alters the sensor's original function, making them excellent candidates for high signal-to-noise ratio sensors. For instance, Au, Ag, and Pd nanoparticles have been reported to fabricate high-performance film sensors that exceed the performance of those without these nanoparticles in the detection of various gas molecules [19,52,61].

2.2.3. Metal Oxide, Metal Carbides and Nitrides (MXenes), and Other Metal Compounds

Besides metal nanomaterials, nanomaterials built on metal compounds are also very promising. They have shown distinct electronic, mechanical, and chemical properties in response to diverse external stimuli. Although they have been widely investigated for their exceptional properties in other fields, their application in intelligent plant systems is rarely reported. However, according to state-of-the-art technologies, the development of metal compound-based nanomaterials has already shown its potential in intelligent plant systems.

The working principle of metal oxide has been elaborated on in plenty of studies elsewhere [65]. Briefly, the conductivity of semi-conductive metal oxide can be either positively or negatively influenced by the absorbed molecules, depending on the oxidizability or reducibility of the molecules. Generally, oxidizing molecules will lead to an increase in the conductivity of p-type semiconductors, and reducing molecules will lead to an increase in n-type semiconductors' conductivity. A large number of metal oxides, such as ZnO [66], CuO [67], SnO_2 [68], and TiO_2 [69], are typical n-type semi-conductive materials. Many of these metal oxides are fabricated into a thin film on a plastic sheet such as polyethylene terephthalate (PET) or polyimide (PI) to maintain the good flexibility of sensors. The nanostructure of the metal oxide is also very diverse. Nanoparticles, nanowires, and nanoribbons are all decent nanostructures for the improvement of performance. These nano-structured metal oxides can be leveraged in intelligent plant systems to perceive various gas molecules, such as H_2, NO, NO_2, and H_2S, in order to identify the ambient key factors in the environment [65].

Another family of nanomaterials that are promising for intelligent plant systems is metal carbides and nitrides. Herein, we refer to the two-dimensional MXenes, which have a formula of $M_{n+1}X_nT_x$. MXenes are different from metal oxides that are usually three-dimensional. They generally have only several layers of atoms. Their skeleton is constructed by layers of transition metal atoms and carbon or nitrogen atoms. Functional groups, such as -O and -OH, cover the surfaces of the skeleton. After development of over ten years, tens of types of MXenes have been reported experimentally, and over a hundred of them have been demonstrated theoretically [70]. The physical and chemical attributes of MXenes vary dramatically and are dependent on their composition, structures, and functional groups. Consequently, different types of MXenes can be selected specifically for certain applications. The most widely reported MXene is perhaps $Ti_3C_2T_x$, which has high metallic conductivity. It has been reportedly mixed with hydrogel to form ultra-stretchable sensors, which have the potential to monitor plant growth [71]. It has also been reported to fabricate resistive, capacitive, and triboelectric pressure sensors that can quantify external mechanical stimuli for plants [72]. It can be used to sense various gas molecules [73] or even single molecules inside the body [74]. To sum up, the revolutionary 2D MXene has been demonstrated to be an excellent nanomaterial for many physical, chemical, and biological sensors, making it a readily available technology for developing intelligent plant systems [75].

Apart from metal oxide and MXenes, other metal compounds can also be used to fabricate film sensors. For example, researchers have demonstrated a multi-modal sensor fabricated using $ZnIn_2S_4$ (which is an important semi-conductive sulfide) that can monitor the illumination as well as humidity of the ambient environment [76]. Metal–organic frameworks (MOFs) are also an emerging group of materials that possess unique light sensitivity, catalyzation, and carbon dioxide capturing properties [77–79].

2.3. Polymers

Polymers are derived from the polymerization of large amounts of organic monomers or oligomers. Compared with metals and nanomaterials, most of them demonstrate improved characteristics as substrates or packages of biosensors for a plant's physiological detection, such as being gas permeable, easy-to-process, lightweight, biocompatible, mechanically flexible, and optically transparent [80]. However, the vast majority of polymers are naturally insulating; usually, they cannot be utilized as active materials in soft film sensors. There are two approaches to dealing with this problem. One is to embed conductive metal or nanomaterials into the polymers to form conducting polymers until the content of the additive exceeds the percolation threshold. The other is to develop naturally conductive polymers, including conjugated polymers and ionically conductive hydrogels. Delocalized π electrons realize the former conductivity in polymers, and the latter is achieved by free-moving ions.

According to the aforementioned physiochemical properties, we mainly discuss three categories of polymers in this section. Two of them are active materials, namely, conjugated polymers and ionically conductive hydrogels. The reason why they can serve as active materials and how they can be used are also discussed. The other category is insulting polymers, which are generally adopted as substrates to protect and insulate the inner functional parts of sensors.

2.3.1. Conjugated Polymers

Conjugated polymers (CPs) are organic macromolecules that are characterized by a carbon backbone of alternating double- and single-bonds, whose overlapping p-orbitals create conjugated pi bonds that are also called delocalized π bonds [81–83]. π electrons are delocalized and spread out in this region to form delocalized π electron clouds and are easily influenced by external molecules or physical fields, which endow CPs with good electrical properties. Due to the migration of carriers along conjugated pi bonds under an applied electric field, CPs demonstrate electrical conductivity, and doping will further enhance the conductivity of CPs [84,85]. Recently, due to the increased awareness of this conductivity, CPs such as polyacetylene (PA), polypyrrole (PPy), polyaniline (PANI), and poly (3,4-ethylenedioxythiophene) (PEDOT) have attracted broad interest in film sensor applications [86,87]. Moreover, in biological systems, especially in plants, the transfer of information between cells is accomplished through ionic transport in plasmodesmata. Therefore, CPs that can accommodate electrical and ionic transport play a significant role in biosensors for plants. Moreover, they have great benefits in terms of biocompatibility, high flexibility, thin thickness, and oxide-free interfaces with aqueous electrolytes [88].

In terms of molecular structure, polyacetylene (PA) is the most straightforward conjugated polymer, making it the prototype of conducting polymers [83,87]. PA was known as a black powder with a conductivity of 10^{-9} S·cm^{-1} in the early stages [89]. Later, in 1977, Shirakawa, MacDiarmid, and Heeger reported that halogen-doped PA shows high electrical conductivity (3×10^4 S·cm^{-1}), which led to the 2000 Nobel Prize in Chemistry [84,90]. In 1980, Edwards and Feast employed another approach to synthesizing PA by preparing a soluble, stable, and well-characterized precursor polymer [91,92]. Finally, the rapid emulsion, dispersion, and suspension polymerization of vinyl monomers in aqueous media offers an approach to fabricating PA-based thin films.

Polypyrrole (PPy) is a heterocyclic and positively charged conducting polymer with an oxidized nitrogen-based backbone that exhibits good electrical conductivity (10^3 S·cm^{-1}) with metals in the form of thin films or bulks. Moreover, PPy was also the first conjugated polymer to be made as a conductive organic thin film [93]. Typically, chemical or electrochemical doping can enhance the conductivity of PPy. During doping, PPy is oxidized, and a π electron is removed from the carbon chain. However, when the PPy is overoxidized, it will lose its conductivity [90]. Notably, PPy also has the best biocompatibility and demonstrates easy immobilization of various biologically active compounds. Hence, it is used mostly in biosensors to detect bio-analytes at a physiological pH and even DNA [84]. Moreover, a flexible pressure sensor based on PPy–cotton composites was reported to show a low detection limit (about 50 Pa), in which PPy was grown in situ on cellulose fibers of cotton pads [94].

Polyaniline (PANI) is mainly composed of alternating structures of phenylenediamine (reduction) and quinone diamine (oxidation) units, which is also called a polyaniline intrinsic state. It exhibits various compositions, structures, colors, and electrical conductivities due to the change in oxidation degree [95,96]. Unlike the doping mechanism of most other polyaromatics, there is no change in electron numbers during doping. The decomposition of doped protonic acid produces H^+ and p-anions (such as Cl^-, sulfate, phosphate) into the main chain, which combines with N atoms in amine and imine groups to form polarons and dipoles, thus leading to PANI's high electrical conductivity. Hence, such a unique doping mechanism makes the doping and de-doping of PANI completely reversible. The degree of doping is affected by various factors, such as pH and potential. Therefore, PANI has good electrochemical activity and electrochromic properties [95,96]. Moreover, the electrical conductivity of PANI depends on the degree of oxidation and doping, and the fully oxidized state in PANI is non-conductive [95,97]. Finally, in terms of PANI synthesis, aniline oxidation is the most commonly used route, which can be accomplished electrochemically or chemically. The former involves the oxidative polymerization of aniline on the anode in an electrolyte solution to produce a PANI film adhering to the electrode surface; the latter involves the oxidative polymerization of aniline monomer with an oxidizing agent in an acidic aqueous solution [98,99].

Poly (3,4-ethylenedioxythiophene) (PEDOT) is a polymer of EDOT (3,4-ethylenedioxy thiophene monomer) that has the advantages of a low energy gap, low electrochemical doping potential, short response time, and good stability, thus contributing to its broad application in organic conductive materials [100]. The commonly used methods for polymerization are electropolymerization, oxidative chemical vapor deposition, and vapor phase polymerization. PEDOT nanoparticle dispersions are usually prepared by aqueous oxidative polymerization of 3,4-(ethylenedioxy)-thiophene with iron (III) salts or peroxodisulfate in the presence of polyelectrolytes, steric stabilizers, or low-molecular-weight surfactants. Moreover, nonaqueous dispersions of PEDOT were generated by ion exchange of the counterions of the stabilizing polyelectrolyte [101]. Additionally, the high polarizability of sulfur atoms in thiophenes leads to a stabilization of the conjugated chains and to excellent charge carrier transport, which leads to special conductive and optoelectronic properties (for example, the conductivity of PEDOT film reaches up to 1420 S/cm) [102]. Among conjugated polymers, due to good conductivity and stability, PANI and PEDOT are the most widely used materials for fabricating various film sensors. Gong et al. reported a piezo-conductive sensor fabricated from a semiconducting polymer, PEDOT, doped with tosylate ion (Tos) thin films, which exhibits a negative piezo-conductive effect [103].

2.3.2. Ionically Conductive Hydrogels

Ionically conductive hydrogels (ICHs) are water-abundant polymer networks with porous structures in which a large number of water molecules and free ions are allowed to move freely across the three-dimensional polymer networks [104,105]. The high electrical conductivity of ICHs derives from the high mobility of ions in water, and thus the main purpose of the ICH fabrication process is to introduce more free ions into polymer networks. During manufacturing, some natural polymers, such as agar and gelatin, can form gels through physical heating–cooling methods. In addition, other natural polymers require cross-linking with ions (Fe^{3+}, Ca^{2+}, Li^+) to form hydrogels, such as alginate, κ-carrageenan, and hyaluronic acid. Moreover, water contained in hydrogels plays a key role in the hydrogel systems being solvent, rendering hydrogels good ionic conductors. Therefore, material systems with the ability to generate free ions in water can be broadly classified into three categories: acids (e.g., HCl, H_2SO_4, H_3PO_4), metallic salts (e.g., NaCl/Na_2SO_4, KCl, LiCl, $LiClO_4$, $FeCl_3$/$FeNO_3$, $CaCO_3$/$CaCl_2$, $TbCl_3$, $AlCl_3$), and ionic liquids (e.g., 1-ethyl-3-methylimidazolium chloride). Based on the above principles, there are two common approaches to enhancing their ionic conductivity: (1) fabricating polyelectrolyte networks to enhance free ion transport and (2) constructing ion channels in hydrogel networks for ion transport. Notably, compared with electronic conductive hydrogels, ICHs are usually transparent, stretchable, tissue-adhesive, and self-healable [21,106–108], which are highly necessary properties for energy storage and conversion devices such as actuators and nanogenerators, as well as for transparent devices such as displays and touchpads [104].

Polyzwitterionic polymers have both cationic and anionic charges on the same macromolecule, which can be used to allow for high ionic conductivity [109]. For instance, Xie et al. developed a class of zwitterionic gel electrolytes that could achieve superior electrochemical performance in solid-state supercapacitors. The zwitterionic nature of poly (dimethylammonium propyl methacrylamide propionate) (PPDP) not only provides strong water retention for this gel electrolyte through the combination of about eight water molecules around the charged groups, but also brings ion migration channels for the electrolyte ions, leading to better electrochemical properties [110].

Qi et al. [111,112] introduced LiCl into a single-network PAM hydrogel. Interestingly, the dissolved Li^+ and Cl^- interact with the water molecules in the hydrogel to form hydrated ions. Unlike free water molecules, hydrated ions require more energy to evaporate. Therefore, lithium chloride can be used to reduce the drying rate of hydrogels. By using the same mechanism and similar strategies, inorganic salts such as sodium chloride, potassium chloride, and calcium chloride are often added to hydrogels. Apart from forming hydration ions, the added salts in hydrogels have been reported to demonstrate the salting-out phenomenon caused by the Hofmeister effect [113,114]. The Hofmeister effect causes hydrogels to be able to form intermolecular hydrogen bonds; electrostatic interactions lead to the formation of sodium/lithium bonds. Thus, the interaction of Na^+ and Cl^- ions with the polymer chains results in a stable charge transfer channel. According to the Hofmeister effect, sodium chloride leads to a salting phenomenon that endows the hydrogel with better mechanical properties and stability.

2.3.3. Insulating Polymers as Substrates

To address the challenges and limitations of using metals and ceramics as substrates and packages, such as low biocompatibility, difficulty integrating wireless radio frequency components, and low softness, insulating polymers have been widely utilized since they offer various possibilities for realizing substrates that are biocompatible, optically transparent, lightweight, easy-to-process, and highly mechanically flexible [80,115]. Particularly, insulating polymers and hydrogels demonstrate some interesting characteristics, including transparency [116], stretchability [117], wearability [22], biodegradability [118], and even self-healing properties [119], which play an irreplaceable role in plant electronics. Candidate polymers include epoxy, polydimethylsiloxane (PDMS), polyimide (PI), and polyurethane (PU) [80].

Polyimide refers to a class of polymers containing an imide ring (-CO-NR-CO-) on the main chain. Benefiting from high electrical resistivity, high dielectric strength, and high temperature resistance, PI has been broadly utilized in microelectronics and film sensors for excellent stability. Moreover, PI film with a certain degree of softness can be bent randomly and stretched harshly. Brain et al. developed an 8×8 flexible electrode array on PI films with a 150 μm electrode diameter and 750 μm pitch [120]. The electrode array was implanted in rats for signal recording and reproducible data were obtained over 100 days, realizing high spatial resolution mapping owing to the electrodes' small dimensions and micro-structures. Although PU and epoxy have similar properties to PI, their low stretchability and low transparency limit their application as film sensor substrates for plant surface attachment since they cannot be synchronized with plant growth. Thus, materials with good electrical stability, colorlessness and transparency, and low stiffness are usually required to be the substrates for plant film sensors.

PDMS is an elastomer derived from the polymerization of a backbone of silicon–oxygen linked with two methyl groups [80]. PDMS is the simplest and most commonly used member of the silicone polymer family, with unique physical and chemical properties such as flexibility, heat resistance, processability, tunable hardness, and other desirable properties [121]. A low and tunable Young's modulus (500 kPa-3 MPa) allows PDMS to have good conformability on plant surfaces and good tensile properties to fit plant growth. For instance, Wu et al. reported a method to substantially reduce the Young's modulus of PDMS and enhance its adhesion and tensile properties [122], allowing PDMS-based sensors to adhere firmly to plant surfaces without affecting the growth of plants. Furthermore, PDMS demonstrates nice permeability and transparency, thus ensuring normal plant photosynthesis. Finally, researchers recently demonstrated that modification of PDMS is expected to deal with the delamination problems of multi-layer laminated sensors [123].

3. Fabrication

Based on the materials discussed earlier, technical analysis of their corresponding fabrication techniques is also necessary. Only with proper fabrication processes will these materials function well as a part of sensors. In this section, we introduce the fundamental working principle and its applicability. Some specific techniques can directly fabricate soft, thin film sensors on fragile plants. Generally, several fabrication processes should be performed consecutively to achieve the final sensors (Figure 3).

3.1. Laser Machining

Laser machining is a digital fabrication process that possesses high machining accuracy, programmable control, and wide applicability. Almost all types of common materials (e.g., elastomers, polymers, plastics, metals, and even ceramics) can be treated by laser beams. Therefore, laser machining has been widely used for soft film sensor fabrication. Generally, by programming different types of laser beams (e.g., ultraviolet lasers or infrared lasers) with diverse power densities, the laser machining process can be divided into two types: patterning and carbonization.

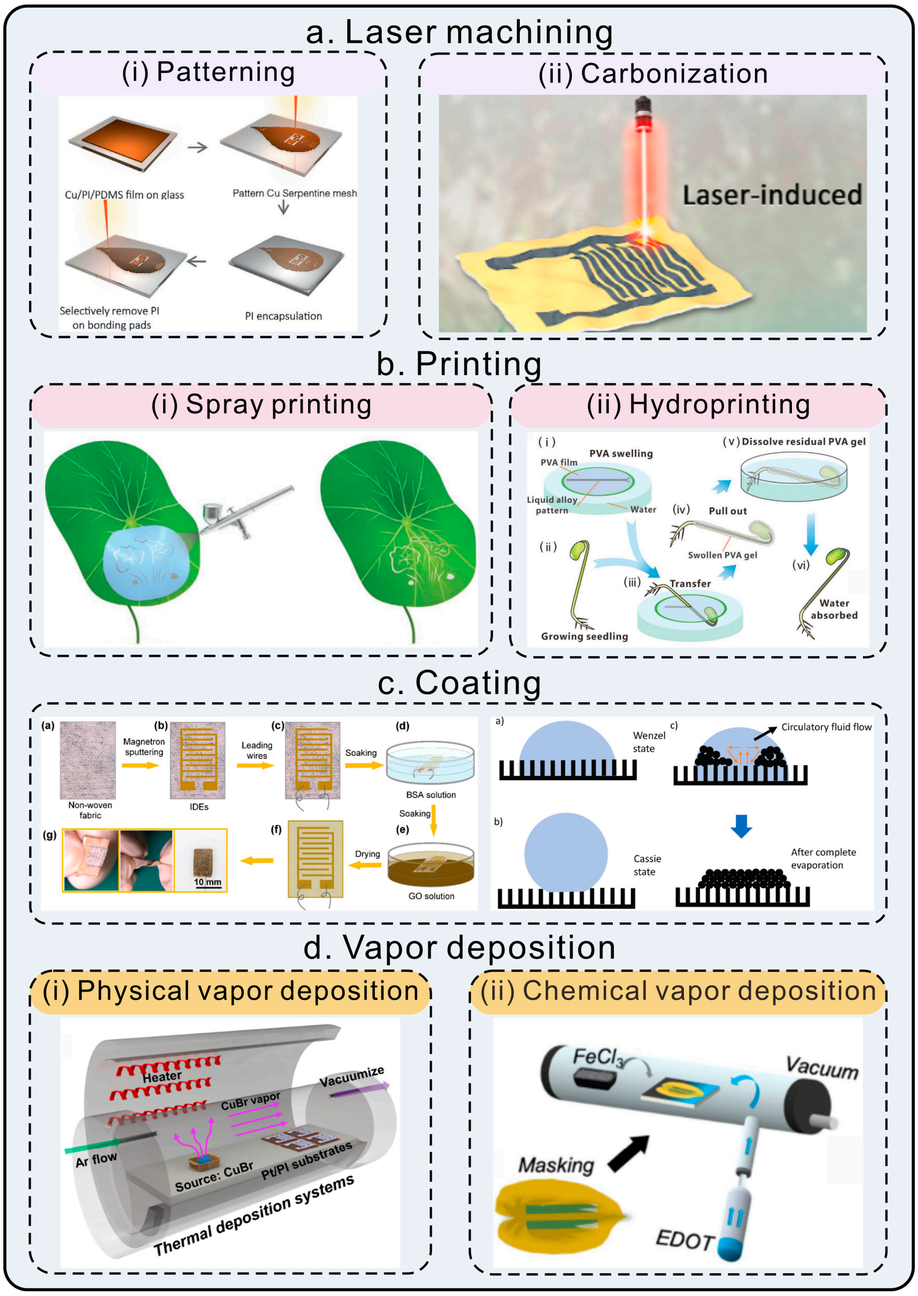

Figure 3. Various fabrication processes for soft film sensors. (**a**) Laser machining. (i) Patterning Cu serpentine mesh (reproduced with permission from [15], copyright © 2021, Wiley-VCH GmbH). (ii) Flexible humidity sensor fabricated by laser-induced carbonization (reproduced with permission from [23], copyright © 2020, Elsevier). (**b**) Printing. (i) Liquid metal wires printed on a lotus leaf via spray printing (reproduced with permission from [31], copyright © 2022, Wiley-VCH GmbH). (ii) Hydroprinting liquid alloy-based morphing electronics on living bean sprouts (reproduced with permission from [16], copyright © 2020, Wiley-VCH GmbH). (**c**) Coating. Left, flexible humidity sensor coated with graphene oxide (reproduced with permission from [124], copyright © 2020, American Chemical Society). Right, a schematic diagram showing the whole process of coating (reproduced with permission from [125], copyright © 2020, Elsevier). (**d**) Vapor deposition. (i) Schematic diagram of CuBr deposited on a Pt/PI substrate with high-temperature air flow (reproduced with permission from [126], copyright © 2018, American Chemical Society). (ii) PEDOT-based plant sensors fabricated via chemical vapor deposition (reproduced with permission from [127], copyright © 2020, Elsevier).

3.1.1. Patterning

Patterning is a convenient process that utilizes laser spots to ablate and cut thin metal films (e.g., Au, Ag, and Cu) into designed circuit patterns. These conductive circuits can then be encapsulated by soft elastomers to form soft sensors. Various pattern structures have been presented to obtain high stretchability and conformability in soft sensors, including self-similar serpentine, origami, and kirigami designs [24]. Here, a few are briefly summarized as follows:

(1) A self-similar serpentine structure is a common pattern that has a meander-shaped layout [128]. When responding to the applied strain and pressure, the serpentine unit can rotate in the plane and buckle out of the plane, significantly reducing the stress distribution of circuits. Therefore, these self-similar networks can be used to connect with rigid chips to form "island-bridge" structures within which to accommodate the mechanical mismatch between components and the elastomer matrix [129].

(2) Origami and kirigami plane patterns are both inspired by paper-cutting arts, which can transfer a flat film to 3D stretchable structures [24]. Using these design strategies, soft sensors can merge a high strain rate (over 300%) with stable conductivity [130,131].

Another feature of laser patterning is selective ablation. As different materials have diverse laser wavelength absorption peaks, researchers can use this property to ablate these materials on demand. Xu and co-workers presented a framework for highly integrated multilayer flexible circuit fabrication [132]. By adjusting the pulse energy of the laser spot, vertical interconnect accesses (VIAs) between different layers can be ablated. Therefore, this fabrication process opens up a new way of achieving highly integrated and multifunctional soft devices.

3.1.2. Carbonization

Laser-induced graphene (LIG) was found in polyimide (PI) films that were carbonized by a CO_2 infrared laser in 2014. This laser-induced carbonization technique provides a relatively more convenient way of obtaining porous graphene structures (from twenty to hundreds of micrometers) and conductive circuits than the traditional chemical vapor deposition (CVD) process [133]. Apart from PI and polyetherimide (PEI) films that are commonly used as LIG substrates, diverse carbon-containing materials (such as cross-linked polystyrene, epoxy, and phenolic resin) can also be converted into LIG. With the help of a 3D laser system, whose focal spot can be adjusted, LIG can be directly fabricated on nonplanar carbon-containing surfaces, including bread, wood, potato, and coconut surfaces. Benefiting from its high electrical conductivity, good hygroscopicity, and convenient fabrication process, LIG has been widely used as an active and conductive material in soft film sensors.

3.2. Printing

3.2.1. Spray Printing

Spray printing provides a convenient process that deposits various inks (such as LM [31], dielectric elastomer [134], and Ag nanowires [135]) on the substrate. Under high-pressure air flow, LM is atomized to form micrometer/sub-micrometer particles. These LM particles instantaneously oxidize under the air environment. In addition, the oxide skin of LM particles helps them adhere easily to various substrates (such as rubbers, papers, and leaves). After removing the thin film mask and redundant LM, soft circuits are printed on the target substrates. The line width and spacing distance of LM traces can be adjusted using a shadow mask. However, due to the high surface tension of LM, the resolution of LM traces is limited. Wang et al. proposed a high-resolution (20 μm), high-density, and high-precision spray technique for thin LM film fabrication [136]. The bulk LM was dispersed by a sonicator to generate micro/nanoparticles, which more easily passed through the gap in the mask and then deposited on the substrate. Zhang et al. presented a conformal mask that can attach to a morphing surface to achieve dynamic printing [137]. Using such a technology, LM circuits can be printed on any 3D arbitrary surfaces.

Although direct spray printing can fabricate LM circuits on most surfaces, hydrophobic surfaces greatly repel LM droplets from forming traces. In nature, lotus has micro-nano structures on its leaves that present super-hydrophobic behavior. To tackle this challenge, Jiang et al. introduced a surface tuning method to print LM circuits on lotus leaves [31]. They utilized a low-concentration soap solution as an intermediate layer on super-hydrophobic surfaces to enhance LM wetting behavior. After that, the LM could be spray-printed on the lotus leaf surface.

3.2.2. Hydroprinting

Hydroprinting, or water transfer printing, is a gentle surface patterning technique for transferring 2D patterns to 3D surfaces [138]. The functional conductive patterns and components are integrated into a water-soluble carrier film (such as polyvinyl alcohol, PVA). When placed on the water surface, the sacrificial film dissolves, leaving only the functional layer floating on the water. Dipping the target 3D object into water and then lifting the object, patterns and components can be transferred to the object's complex surface. Furthermore, with the help of an optical scanner and computer design, 2D-printed patterns can be tailored to conform well to the shape of 3D objects. Most recently, various conductive materials have been used to transfer curved circuits, such as aluminum ribbons [139,140], silver nanoparticle-based ink [141], graphene [142], and LM. Additionally, with particle-assisted sticking, ultrathin Ag-In-Ga patterns can be directly printed on surfaces such as skin and gloves as an "electronic tattoo" [143]. Benefiting from its conformability, stretchability, and comfortability, this electronic tattoo attaches well to human skin for electromyography signal acquisition. To further explore the application potential of this method, Jiang et al. utilized hydroprinting technology to print LM circuits on fragile and fast-growing plant epidermises, such as rose petals, leaves, and bean sprouts [16]. In short, the hydroprinting process provides a convenient and gentle process for complex 3D surface circuit printing and has wide potential for epidermal electronics for plants.

3.3. Coating

Coating, which is usually used to fabricate thin layers of materials, is a fabrication technique that is simple, widespread, and easy to learn. The materials that can be fabricated by coating are diverse and include various active materials, substrate materials, and electrodes. These materials are usually dissolved in solvents that are removed later. Consequently, the coating materials are generally dispersions of nanomaterials and mixtures of polymers. These liquid materials have to be evenly dispersed to ensure the final quality of the formed layer. There are several representative sub-categories for coating, among which drop casting/coating, spin coating, and spray coating are frequently adopted in the fabrication of thin film sensors.

Drop casting directly coats a thin layer of material on its underlying structures. After the drop of a liquid solution, the solution flows and fills the structure to be coated. Spontaneous or forced evaporation is then applied to remove the solvent, after which a thin film is formed. For example, the drop casting of SWCNT aqueous solutions [46], PVA solutions [144], and GO micro-flake dispersion [145] has been reported to form functional layers. In order to fabricate a thin layer using the drop casting technique, a mask with a defined shape is required. For instance, Ag nanowires dispersed in ethanol were drop cast on a mask and dried under a vacuum to fabricate electrodes with a rectangular shape [63]. Although drop casting is a rapid and useful method for the fabrication of thin films, the evaporation process can easily lead to an uneven distribution of nanomaterials mixed within the solution as the coffee ring effect can alter the distribution of these nanomaterials [125].

Compared with drop casting, spin coating can create relatively even and smooth films. Leveraging viscosity, the coating materials are dropped on a spin surface and then sheared thin to maintain the centripetal force. Many substrate materials [46,63] and functional materials [146] can be fabricated by such a method. In the processing, the thickness of fabricated films depends on the spinning time and viscosity of materials. However, an inadequate spinning time may result in an uneven surface on the fabricated films. In this case, several rounds of spin coating can be performed to obtain a thin film with the required thickness and surface flatness [147]. Another coating method that is frequently adopted in the fabrication of thin film sensors is spray coating. Similar to the technique of spray printing, droplets of dispersion are sprayed from a nozzle and re-fused together on the sprayed surfaces. After the spray process, the solvent-sprayed materials are evaporated to form functional films [59]. Different shapes of fabricated films can be obtained through mask-based spray coating [19], and fabrication precision is obviously therefore determined by the precision of masks.

3.4. Vapor Deposition

Vapor deposition is a series of techniques that can fabricate functional thin films on target surfaces using physical processes or chemical reactions. Both organic and inorganic materials can be fabricated by these techniques. Due to the distinct properties of materials, different vapor deposition techniques should be selected accordingly. From the perspective of working principles, vapor deposition is categorized into physical vapor deposition and chemical vapor deposition.

3.4.1. Physical Vapor Deposition

Physical vapor deposition (PVD) encompasses a variety of techniques that gasify the source material and deposit it on target substrates. Generally, the source materials are metals, alloys, and their compounds. During the heating process, they are evaporated from the bulk source material and then deposited on the target substrate in a low-pressure atmosphere. The target substrates are usually substrates for thin film sensors, such as PI [145] and PDMS [148]. Commonly used PVD techniques for thin film sensors include thermal evaporation, electron beam evaporation, and sputtering. Thermal evaporation uses a very large direct current to resistively heat the high-melting-point boat or coil for the direct evaporation of source materials. Due to direct heating, low-boiling-point material, such as Ag [148] and CuBr [126] should be used in this method to avoid melting the boat or coil. The heating of electron beam evaporation is relatively localized. By giving off accelerated electrons from an electron gun, the source materials are struck and heated into a gaseous phase. The gaseous materials are then deposited on the target substrate. Source materials such as Au [149], Al_2O_3, and CeO_2 [126,150] have been used to fabricate various gas detection sensors through electron beam evaporation. The working principle of sputtering is similar to electron beam evaporation to some extent. By ionizing and accelerating particles to strike the source material, atoms on surfaces are dislodged from the bulk source material and oriented to the target substrate for deposition. Compared with other PVD techniques, sputtering, especially magnetron sputtering, can achieve relatively uniform thin films with fewer defects. Plenty of materials for electrodes and functional layers, such as Au [151], Chromium (Cr) [60], titanium (Ti) [152], and ZnO [145], have been reportedly used for thin film fabrication via sputtering. Similarly, for high precision and better shape control, masks can be used in the process of PVD to avoid the unnecessary deposition of source materials.

3.4.2. Chemical Vapor Deposition

Different from PVD, chemical vapor deposition (CVD) involves chemical reactions of gaseous phase precursors. Taking the reaction conditions of the gaseous phase precursors into consideration, there are several variations in CVD types. However, the basic reaction processes of these CVDs are almost identical. The fundamental process usually includes absorptions of gaseous reactants or intermediate products of reactants, reactions at the gas–solid interface, and desorption of unreacted species and gaseous products [153]. After these three steps, a continuous thin film is finally coated on different substrates with various surface topographies. In contrast to PVD, which is a so-called line-of-sight deposition technology, CVD is volumetric and does not require a direct line-of-sight between the target surface and the source material. This makes CVD more advantageous when fabricating thin coatings on micro/nano-structured surfaces. Both organic and inorganic thin films can be deposited using the technology of CVD. One of the most prevalent groups of materials that has been reportedly fabricated by CVD is carbon-based nanomaterials, which refers to CNTs, graphene, and graphite. Leveraging the carbon solubility and morphology of different materials, different carbon skeleton structures can be fabricated accordingly. Nanoparticles of Fe, Cu coils, and Cu-Co alloys facilitate the deposition of SWCNTs, graphene, and graphite, respectively, which shows the ability of CVD to fabricate all-carbon thin film sensors [47,154,155]. Apart from these nanomaterials, CVD can also be used to fabricate thin polymer layers. The low growth temperature and solvent-free nature of CVD make it a promising candidate technology for the functional coating of fragile objects such as plants [153]. For instance, Andrew's group has developed a set of CVD equipment for the direct functional coating of plants. The deposition of p-doped conducting polymer, PEDOT-Cl [127,156] and PProDOT-Cl [157], shows the potential of CVD to fabricate organic conductive electronics on plants directly. In addition to the above conductive or semi-conductive materials, insulating materials such as parylene [151,158,159] can also be fabricated by CVD.

4. Applications

4.1. Physiological Detection

Wearable soft film sensors can directly attach to the plant's surface and provide a precise and gentle sensing approach. This technique can detect various real-time data relating to plants' growth status and living microclimate. Thus, these soft film sensors can help us investigate plant physiology. This technology can be generalized in intelligent and precise agriculture, smart horticulture, botanical research, and so on (see Figure 4).

4.1.1. Plant Growth Status

Real-time monitoring of a plant's growth or development status, such as stem height, leaf length, and bending angle, is highly significant for plant physiological prediction. Traditional rigid sensors do not attach well to the growing parts of plants. However, soft film sensors can solve such a problem commendably. For instance, the plant's growth states can be monitored by a stretchable resistive strain sensor, whose resistance will change as the plant tissue grows. A carbon nanotube (CNT)/graphite sensor was previously attached to the plant surface to obtain growth information quantitatively. Moreover, this soft film sensor captured the rhythmic growth of the fruits of Solanum melongena L. and Cucurbita pepo [160]. Hsu et al. developed an ultra-thin wearable sensor for aloe leaves and an elastic band sensor for peppers based on a multifunctional dual-network (PAA-RGO-PANI) hydrogel. Further, it can also be used as a supercapacitor for energy storage [161]. Jiang et al. presented a hydroprinted liquid alloy-based morphing electronics (LAME) process for monitoring highly dynamic plant growth. Due to the wonderful compliance and deformability of liquid alloy circuits, LAME could monitor the water content and length of leaves. This LM-based soft sensor lays the foundation for researching new flexible deformable electronics for plant robots [16].

Stem flow is also a key feature for analyzing plant health, crop cultivation, and water relations. Chai et al. developed a flexible electronic sensor that could harmlessly coexist with plants and continuously monitor stem flow. Sensors were installed on stems and branches near the watermelon and recorded water flow during periods of light and darkness. These findings suggest that the accumulation of fresh fruit weight occurs primarily at night, disrupting the traditional understanding of plant growth. This sensor has a wide range of potential applications in monitoring the health of plants for agricultural production [15].

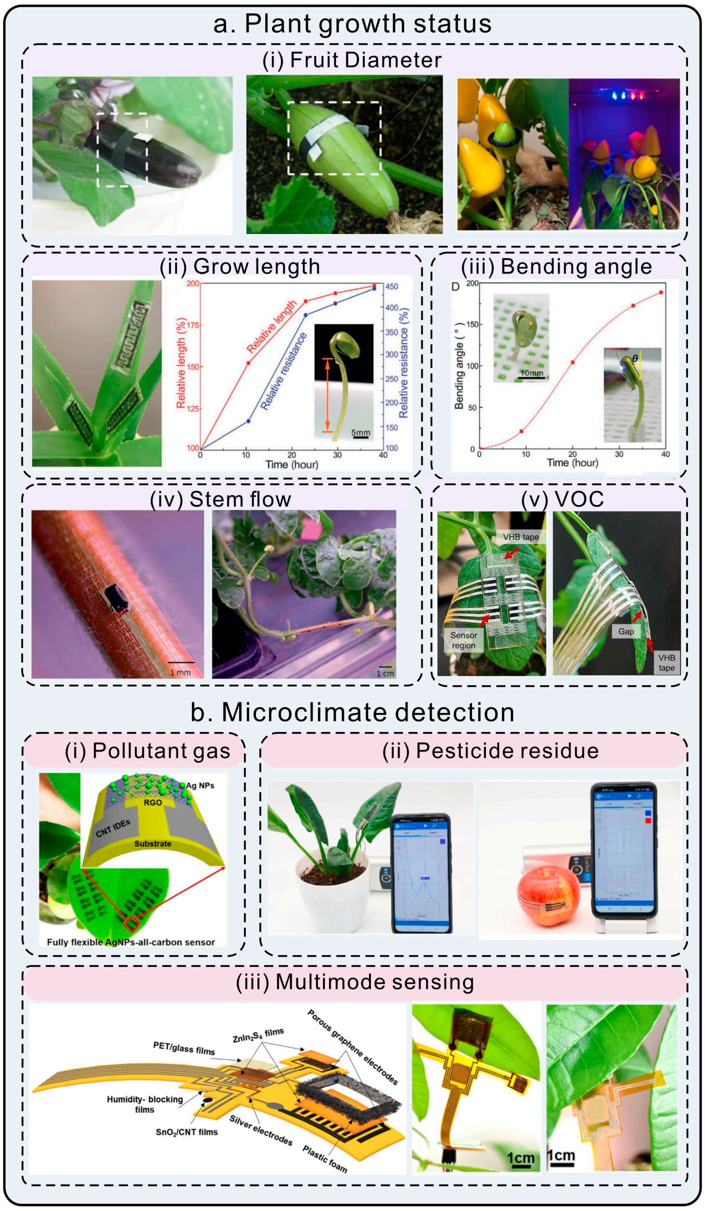

Figure 4. Soft film sensors for plant physiological detection. (**a**) Detections of plant growth status. (i) Fruit diameter detection. Left and middle are reproduced with permission from [160], copyright © 2019, Elsevier. Right is reproduced with permission from [161], copyright © 2021, Elsevier. (ii) Grow length detection. Left is reproduced with permission from [161], copyright © 2021, Elsevier. Right is reproduced with permission from [16], copyright © 2020, Wiley-VCH GmbH). (iii) Monitoring the sprout's bending angle (reproduced with permission from [16], copyright © 2020, Wiley-VCH GmbH). (iv) Sensors for recording plant stem flow (reproduced with permission from [15], copyright © 2021, Wiley-VCH). (v) Detection of leaves releasing VOCs (reproduced with permission from [63], copyright © 2021, Elsevier). (**b**) Detection of the microclimate around plants. (i) Detection of pollutant gas surrounding leaves (reproduced with permission from [19], copyright © 2018, American Chemical Society). (ii) In situ analysis of pesticide residue on crop surfaces (reproduced with permission from [52], copyright © 2020, Elsevier). (iii) Multimode sensing for diverse environment parameters, including light, temperature, and humidity (reproduced with permission from [76], copyright © 2020, American Chemical Society). Left: schematic of the detailed device structures with different functional components. Middle and right: back and front sides of a multimodal flexible sensor device attached on the bottom side of a leaf.

The volatile organic compounds (VOCs) emitted by plants are often used for protection or to communicate with other organisms. Light, temperature, and environmental factors (e.g., nitrogen deposition, ozone concentration) can affect the rate of VOC emissions from plants. Li et al. developed an attachable VOC sensor on leaves for real-time analysis of plant volatiles. The sensor was resistant to mechanical disturbances such as wind blowing or hand touching. It was mounted on the surface of tomato leaves and could classify 13 plant VOCs accurately. Moreover, the sensor could detect mechanical cuts at different locations on the tomato plants to detect plant disease infections, thus providing a solution for long-term, real-time plant health monitoring [63].

4.1.2. Microclimate Perception

In addition to growth conditions, external environmental factors can also affect a plant's health (e.g., toxic substances, pollutant gases, temperature, humidity, and light). Li et al. reported a sprayed NO_2 sensor with ultra−high sensitivity that could monitor toxic gases. This flexible and sensitive sensor provides a new option for the real-time monitoring of toxic gases and human−computer interaction [19]. Zhao et al. developed a wearable biosensor that meets rapid and nondestructive detection demands. The sensor could significantly observe pesticide residues on the plant surface and provide early warnings at characteristic moments. This work provides a new way of thinking about how to obtain information related to pesticide residues [52]. Lan et al. developed a highly sensitive GO-based soft humidity sensor. The entry of water molecules between the electrodes changed the magnitude of capacitance, and the humidity change on the leaf surface could thus be measured [23].

Furthermore, there are many integrated sensors for multiple different factors to monitor. Another butterfly-shaped sensor was dispersed in the field as if it were dandelion seeds, receiving data wirelessly via Bluetooth. It monitored temperature, humidity, and strain measurements and had great potential for the future monitoring of crops in large farms [152]. Yin et al. used designed sensors to study the fertilization of corn fields. They revealed that fertilized plants had higher humidity and lower temperature than unfertilized plants [162]. Lu et al. designed a multimodal plant healthcare flexible sensor system to measure humidity, light, and temperature in real-time for plant growth management. The sensor system was flexible and lightweight, could respond quickly to light illumination, and was capable of stable and long-lasting humidity sensing [76].

4.2. Intelligent Plant-Hybrid System

In recent years, researchers have been trying to combine soft sensors with plants to generate intelligent plant-hybrid systems. As mentioned above, plants have abundant natural intelligent abilities, yet we still have not fully explored them. To cope with this challenge, the soft film sensor acts as a bridge to connect with plants and artificial intelligent systems. We currently divide intelligent plant-hybrid systems according to three aspects: energy harvesting, human–plant interaction, and plant manipulation (Figure 5).

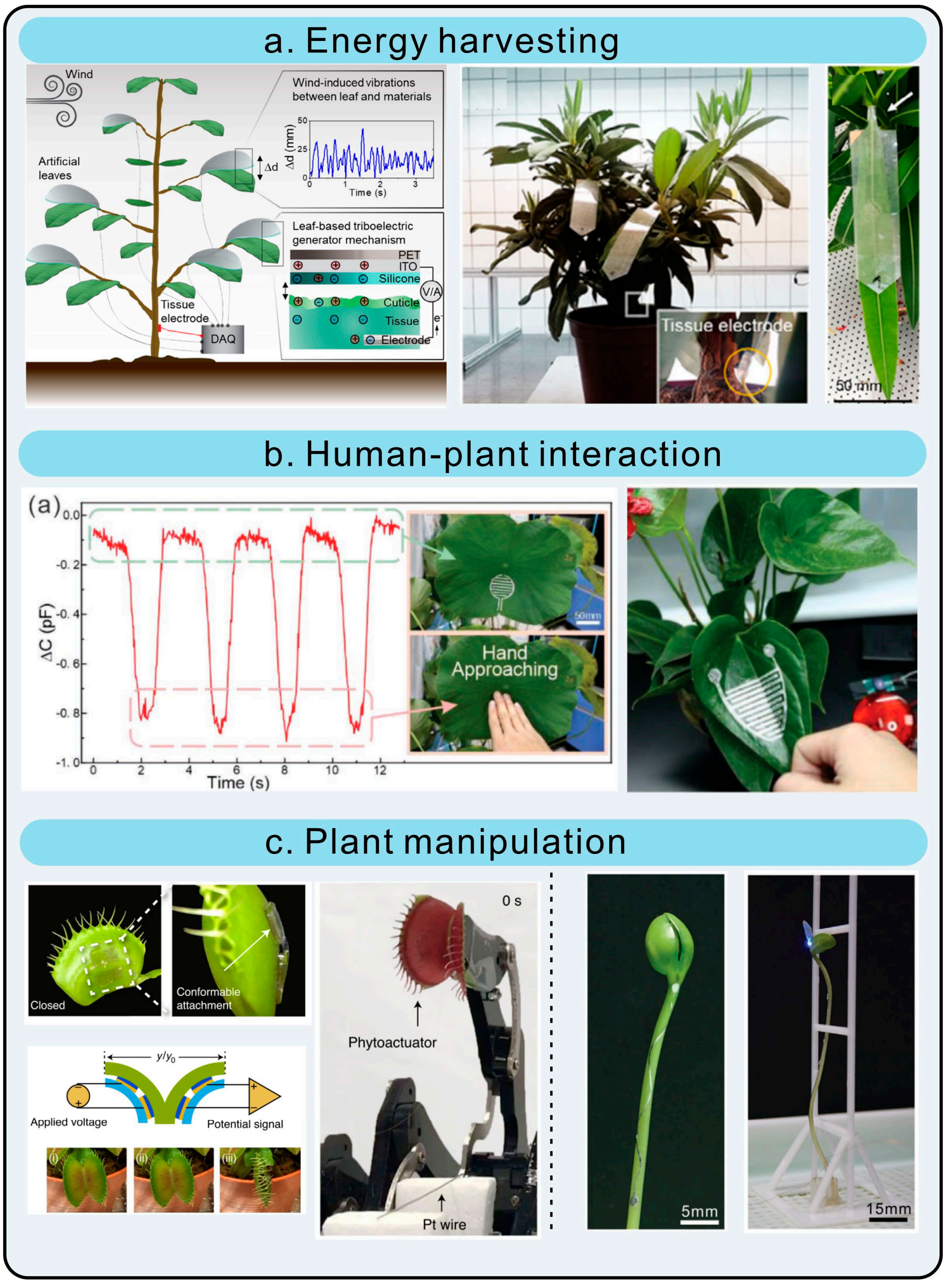

Figure 5. Plant-hybrid systems. (**a**) Energy harvesting system that converts wind energy into electricity (reproduced with permission from [163], copyright © 2020, Wiley-VCH GmbH). (**b**) A human–plant interaction system that can sense hands approaching (reproduced with permission from [31], copyright © 2022, Wiley-VCH GmbH). (**c**) Living plant manipulation systems. Left: manipulating a flytrap to grasp a thin Pt wire (reproduced with permission from [164], copyright © 2021, Springer Nature). Right: manipulating a bean sprout to climb a ladder (reproduced with permission from [16], copyright © 2020, Wiley-VCH GmbH).

4.2.1. Energy Harvesting

Harvesting energy from the environment and natural resources in green and carbon-neutral ways is essential for responding to the global energy crisis. In particular, wind energy has been widely investigated. Plant-hybrid energy conversion systems have been established to transfer wasted random and low-power wind into electricity. Blown by wind, plant leaves vibrate and come into contact with assembled triboelectric nanogenerators (TENGs), generating voltage potential [165]. Moreover, these TENG films can couple to form soft sensor arrays to detect wind directions [163]. This harvesting power can also be used to supply power for other soft sensors of plants [166].

4.2.2. Human–Plant Interaction

For a long time, people have looked at plants as essential ornaments in their offices and living rooms. Plants in those places can not only provide fresh air, but also cultivate people's emotions and relieve stress. However, the interaction between plants and humans is unidirectional, and only people can sense the existence of plants. To overcome such a challenge, liquid metal-based soft film sensors were placed on plant surfaces to build a bridge of interaction between humans and plants [31]. With the help of soft sensors, this plant-hybrid system can detect human approaches and gestures by recording the capacitance changes in the sensor. In that case, inconspicuous plants can be used as intrusion sensors for security. When thieves approach and go by, these plants can detect them and sound the alarm. Moreover, these plants can act as biological controllers that function as traditional mechanical switches to control appliances such as lights, fans, and computers in the home. These demonstrations pave the way for human–plant interactions.

4.2.3. Plant Manipulation

Plants have a range of sophisticated features/capabilities, including continuous growth, rapid response, and unique climbing abilities. To take full use of these fascinating features, researchers have shown great interest in manipulating plant behavior on-demand, with two key challenges existing.

The first is the creation of a physical interface that allows for communication with plants. During the growth and action of plants, electrophysiology phenomena occur when plants receive stimulations [167]. In the 19th century, Sanderson found electrical signals in Venus flytraps when their trap closed. Identifying and characterizing electrical pulses would take a significant step toward understanding plants' physiological behavior. However, traditional surface potential measurement methods use rigid electrodes (e.g., Ag/AgCl electrodes) to puncture tissues, which would damage the health of plants. Plant-conformable soft sensors provide a new way of measuring plants' intrinsic electrical signals. These conformal sensors can be attached to the surface of Venus flytraps for long-term recording (over 10 days) [168]. After understanding the mechanism of sense response, these soft electrodes can also be used to apply an external electrical pulse to modulate the flytrap's behavior [164]. Combining a phytoactuator with a robotic arm, the plant-hybrid system can pick up a fine wire and capture moving objects.

The second challenge is to accommodate the fast growth of plants. With cell division, differentiation, and enlargement, the surface and morphology of plants will change. Although most soft sensors possess good flexibility and stretchability, these sensors' substrates still restrict the growth of plants. To tackle this challenge, LM-based soft sensors can be directly hydroprinted onto the surface of plants without carrier films [16]. During the rapid growth process of bean sprouts, such LM circuits remain conformable and pinned on the epidermis of the sprout and morph with the dynamic stretching and deformation of the hypocotyl. These LM-based soft circuits can manipulate the growth orientation of bean sprouts, exploiting the plant's phototropism. By controlling the emission of LEDs placed on the cotyledon, the growth angle of the sprouting seedling can be turned and the sprout can climb a ladder.

5. Conclusions and Perspectives

Plants are amazing biological systems that have abundant natural intelligence. Based on soft film sensors directly attached to plants, various biological information from plants can be precisely transferred to digital signals. Moreover, with the help of soft film sensors, artificial intelligence technology can be closely connected with plants' natural intelligence, forming intelligent plant systems. As mentioned above, soft film sensors have broad applications in monitoring plant physiological information, such as microenvironments, growth status, and crop yield and quality. The information collected from plants can be used as indicators for the settings of intelligent plant management systems, enabling a new level of precision agriculture, botanical research, and intelligent forestry. Furthermore, plants can be seen as integral machines and can be combined with soft film sensors to establish intelligent plant-hybrid systems related to energy harvesting, plant–human interactions, and plant manipulations. There are still several grand challenges and opportunities to be explored.

(1) Reliable interface matching between soft film sensors and plants. Most existing soft film sensors process soft substrates to adhere to plant surfaces. However, such a bonding strategy can bring about mismatches or detachment due to the rapid and continuous growth of plants. Moreover, tightly attached sensors would hinder plant growth. Therefore, developing a reliable and stable interface between sensors and plants is vital for achieving long-term (months and years) wearable detection. LM provides one of the solutions, which can be directly printed on plant surfaces without carrier films. As LM has unique fluidity and ductility, LM-based sensors can conformally morph with plant growth. Thus, we look forward to further developing the next generation of soft film sensors with a stable attachment interface, lower stiffness, and compatibility with plant growth.

(2) Multi-sensor fusion. Until now, multimode soft film sensors have been developed to monitor diverse physiological information (such as temperature, light intensity, and water transport). However, these sensors are always placed on a single part of plants (e.g., leaves), where information is very limited. Multi-sensor fusion systems that can be integrated into various plant parts (such as leaves, stems, and roots) may provide more comprehensive and rich physiological information.

(3) More intelligent plant-hybrid systems. In the current stage, plant-hybrid systems have shown the potential to take full advantage of plant intelligence in different aspects, such as energy, interaction, and manipulation. We expect to be able to comprehensively integrate these functional parts and thus form highly intelligent plant-hybrid systems. The next generation of plant-hybrid systems will possess a highly efficient transforming mechanism capable of harvesting various forms of energy from nature (such as wind, rain, light, and temperature). Furthermore, plants could potentially interact intimately with humans by, for instance, behaving like "plant pets", where plants can sense human stress and react in a friendly manner to comfort humans by releasing pleasant smells.

With the continuous development of essential materials, advanced fabrication technologies, and cross-disciplinary fields, these goals will definitely be achieved soon with the advent of the era of intelligent plant systems.

Author Contributions: Writing—original draft preparation, Q.J., Z.C., Z.Z. and Z.H.; writing—review and editing, S.Z. and Z.W.; supervision, Z.W.; funding acquisition, S.Z. and Z.W. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Natural Science Foundation of China (52188102), the China Postdoctoral Science Foundation (2021M701311), and the Postdoctoral Innovation Talents Support Program (BX20220126).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The datasets generated and/or analyzed during the current study are available from the corresponding author upon reasonable request.

Conflicts of Interest: The authors declare no conflict of interest.

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